STUDY OF STRUCTURAL BEHAVIOR OF THIN FILMS

SECOND YEAR SUMMARY REPORT

By Frank Feakes and Earl E. Chadsey, Jr.

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SUMMARY

The Second Year Summary Report covers work completed by Norton Research Corporation on the structural properties of boron and boron carbide which had been vacuum evaporated onto thin substrates such as polyimide film and aluminum foil. The work was carried out during the period September 17, 1968 through September 17, 1969. Previous work in a number of programs at N.R.C. had demonstrated that layers of the vacuum evaporated deposit along with the substrate could be bonded together to give multi-layered composite materials which had mechanical properties which were isotropic in the plane of the composite. In general, the earlier work had demonstrated that while the composites gave high values of specific modulus, the composite strengths were lower than anticipated from several indirect methods of measuring the strength of individual films.

The present program investigated a number of procedures aimed at increasing the strength of the composites. The work included examination of the dimensional and weight changes in the polyimide substrate when exposed to the condition experienced during vacuum coating with boron and boron carbide. A detailed examination of the surface morphology of both the polyimide substrate and the vacuum deposited boron and boron carbide indicated that the most important crack nucleating defects appeared to be those associated with "spit marks" and microscopic droplets of molten material embedded in the deposit. Extended vacuum degassing of the polyimide substrate prior to coating did not substantially improve the adherence of the deposits to the polyimide. It did, however, lower the strength of the polyimide and decrease its tear resistance.

The latter part of the program was devoted mainly to the development of procedures for the direct measurement of the strength of films of boron deposited on thin polyimide and metallic substances. Direct tensile tests were also made on small flakes of the deposits. Procedures were developed to carry out depositions at substrate temperatures ranging from about 300^{0}C to 1000^{0}C on specimens suitable for direct tensile testing and the measurement of the stress-strain behavior. The highest strength values measured by these techniques was 131,000 psi by direct measurement of boron carbide flakes and 110,000 psi from analysis of the strain behavior of the experimental boron-titanium tensile specimens. Initial tests aimed at measuring the strength of deposits made on tantalum substrates held at about 1000^{0}C were complicated by tantalum-boron interactions.

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INTRODUCTION

Previous work at Norton Research Corporation had shown that materials such as boron and boron carbide could be vacuum evaporated onto thin substrates such as polyimide film and aluminum foil. (References 1, 2, 3, 4) Multiple layers of the evaporated deposit and substrate could then be bonded together to give a composite material which had mechanical properties which were isotropic in the plane of the composite. The earlier work indicated that the degree of translation of the elastic modulus properties (stiffness) of the boron and boron carbide into the composites was high and in many composites, close to theoretical. On the other hand, while the strength of the composites was relatively low, there were a number of positive indications that the strength of individual thin films could be higher than indicated from composite performance.

The basic purpose of the present program was to investigate a number of procedures which appeared promising for increasing the strength of the composites. This work was divided into two main areas of investigation. The first was concerned with the characterization and improvement of the boron carbide-substrate combination as a reinforcing material. It included work on dimensional changes in and the morphology of the polyimide substrate used for most of the work, as well the effect of vacuum outgassing of the polyimide film. Some preliminary work was also completed on using higher substrate temperatures during the deposition step.

In the second phase of the work more emphasis was given to the study of single elements of the reinforcing material; that is, the actual strength of the boron and boron carbide films. As the work progressed, more attention was given to boron than to boron carbide. The main reasons were:

1) Work on the boron filaments had shown that so called amorphous boron could be made with high strength.

2) High purity boron was more readily available than high purity boron carbide.

3) The possibility existed that variations in the boron-carbon ratio in evaporated deposits of boron carbide would have an effect on the strength of the deposit.

THE CHARACTERIZATION AND IMPROVEMENT OF BORON CARBIDE FILM REINFORCEMENT MATERIALS

The reinforcement materials used in this program were made by passing a thin polyimide (or aluminum substrate) over a high temperature source of boron carbide vapor in vacuum. Boron carbide was then deposited on the substrate as a thin coherent film. Previous work had shown that the strength and stiffness of any composites fabricated from multiple layers of boron carbide and substrate could be related back to the strength and stiffness of the boron carbide film. The form and dimensions of the boron carbide are reproductions of the surface of the substrate. Consequently in order to make a deposit which is smooth, planar and without defects it is important that the substrate being coated also be smooth, flat and without surface imperfections. Since the substrate is also exposed to radiant energy from the high temperature boron carbide source ($> 2600^{0}C$), it is important that the substrate be thermally stable -- from both dimensional and chemical points of view. The initial part of the experimental work of this program was therefore directed towards an examination of the effect of heat in the dimensional characteristics of the polyimide film. This was followed by measurements of weight losses of the film when exposed to elevated temperatures in vacuum. The next phase of work was a more detailed examination of the surface morphology of the polyimide film. The main interest here was to characterize and enumerate the most important surface defects in the polyimide substrate. This work in turn lead to further studies of the crack nucleating defects in samples of

boron carbide which had been vacuum deposited on these polyimide films. This work was of prime importance because of the possibility that the strength of the boron carbide film was limited by defects in the deposit.

Three other general subjects related to process modifications were also investigated. They were modifications which were considered likely to permit fabrication of composites with higher tensile strength.

1) Vacuum oven degassing of the polyimide film prior to installation in the vacuum cooling chamber. The specific purpose of this work was to examine the possibility of improving the adhesion between the boron carbide and the polyimide film.

2) High temperature deposition of boron carbide on both polyimide and aluminum foil substrates. This work was deemed desirable since other evidence had indicated that higher strengths would possibly be achieved if deposits were made at higher substrate temperatures than used in earlier work.

3) Repeated alternate deposition of boron carbide on two sides of polyimide film to gradually build up layers of equal thickness on the two sides. The main purpose of this work was to produce relatively thick films of boron carbide which would be sufficiently flat for direct tensile test measurements.

Each of the above phases of work in this section are summarized below.

Dimensional and Weight Changes of Polyimide Film

Most materials expand when heated and contract again when cooled. This is not necessarily a reproducible change. For example, a material may not return to its original dimensions when restored to its original temperature. Kapton polyimide film was found to be affected assymetrically. For example, a length of 0.25 mil polyimide film was taped to a base and was then sampled by the careful removal of a rectangular section from within its boundaries. This section was placed in a vacuum oven at 350^{0}C for a period of 20 minutes. After the exposure the specimen was allowed to cool to room temperature and was then placed in the opening from which it had been taken. The two dimensions of the rectangular sample were affected differently. The length of the sample in the direction of the main length of the polyimide film in the supply roll was the same as its original length. This coincided with the transport direction in the semi-continuous boron carbide coater and the rolling direction during original film manufacture. The side of the sample perpendicular to the transport direction of the polyimide was shorter than its original length. The reduction in film width was about 2.6%. Dimensional instabilities of the substrate such as this undoubtedly have significant effects on the planarity of film exposed to temperature fluctuations and this in turn affects the flatness of the boron carbide deposited on the polyimide substrate.

In a further experiment relating to substrate stability, two different lots of 0.24 mil polyimide film were also exposed to heat in a vacuum furnace to determine weight losses of this polyimide under process conditions. A five foot long sample of the 9½ inch wide material was taken from each lot. Sample "A" represented material which had been exposed in a vacuum oven for 37 days at 105°C and then for 60 days at room temperature. Sample "B" represented material as received from Du Pont. Both samples were held in room ambient air for two days before the weight loss test was started. The samples were weighed in and out of the furnace for each temperature exposure to determine the change in weight produced. During each exposure period the samples were held at the exposure temperature for one hour. Exposure temperatures were 70°C, 120°C, 250°C, 300°C, 350°C, 400°C, and 450°C. In Figure 1, the sample weight after each exposure is shown plotted against exposure temperature. There is little difference between the two curves. Both samples underwent similar changes. The plateaus at 100°C and 375°C suggest completion of removal of one substance before the start of removal of a second material. The substance removed below 100°C was presumably water. The substance removed between 100°C and 375°C may have been unreacted raw materials such as aromatic diamines and dianhydrides. The more rigorous exposure in the vacuum oven apparently produced no permanent change in the outgassing properties of the material as far as water was concerned. Moisture appeared to be easily absorbed and readily released. The manufacturer's data, shown in Table I and mass spectrograms of the chamber atmosphere both confirmed this. There appeared to be a difference in

Figure 1

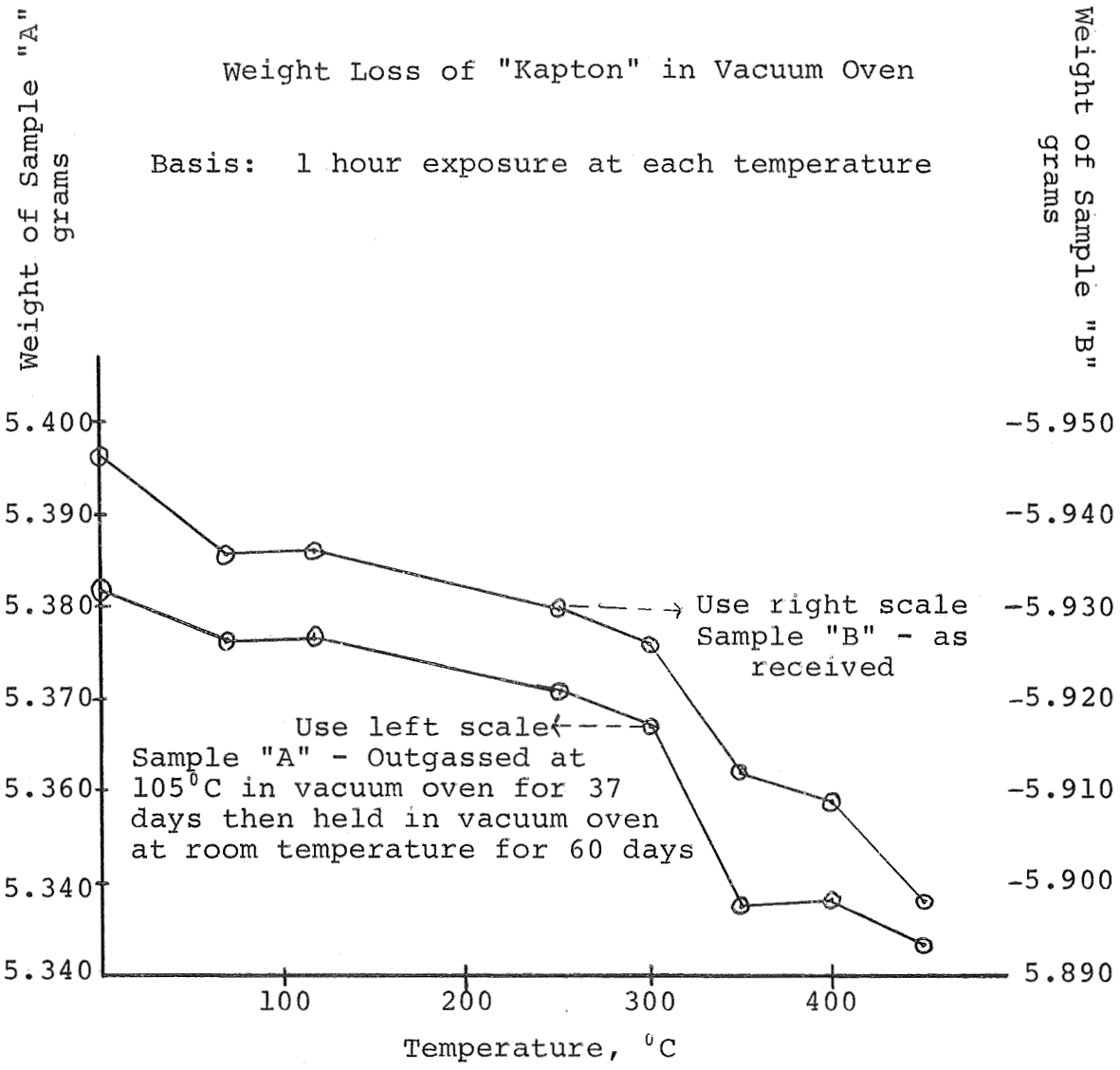

Weight Loss of "Kapton" in Vacuum Oven
Basis: 1 hour exposure at each temperature
Weight of Sample "A" grams
Weight of Sample "B" grams
5.400
5.390
5.380
5.370
5.360
5.340
5.340
-5.950
-5.940
-5.930
-5.920
-5.910
-5.900
5.890
Use right scale
Sample "B" - as received
Use left scale
Sample "A" - Outgassed at 105°C in vacuum oven for 37 days then held in vacuum oven at room temperature for 60 days
100
200
300
400
Temperature, °C

Table I

Rate of Drying Type H "Kapton" at 23°C*

Film Thickness	Time for ½ of Moisture to Leave Film
1 mil	3 minutes
2 mil	10 minutes
3 mil	21 minutes
5 mil	54 minutes

*Data supplied by DuPont

the outgassing rate of the unidentified material driven off in the temperature range from 125°C to 400°C. The "plateau" at 375°C was not flat for Sample "B". This indicated that evolution of one material was not complete before evolution of a second material started. Comparison of the two curves suggested that the vacuum oven exposure removed some of this material. During the entire series of exposures, 0.72% of the material previously exposed to a vacuum oven environment was removed compared with 0.81% of the "as received" material. It is likely that major changes in mechanical properties of the polyimide film produced by the vacuum oven exposure resulted from the removal of this unidentified material which the manufacturer has indicated may be aromatic diamines or dianhydrides.

Further information on the effects of vacuum degassing on the polyimide film is presented on pages 24, 25 of this report.

Morphology of Polyimide Film and Reinforcement Material

Samples of polyimide film and reinforcement material were examined with the optical microscope to determine whether they contained defects which might affect reinforcement strength by nucleating cracks in the boron carbide coating. A defect was considered to be any irregularity in the surface of either the polyimide substrate or the reinforcement.

The polyimide film had many surface defects. The dimensions and frequency of occurrence are shown in Table II. The five major types were:

1) Stretch marks which were parallel with the rolling direction of the film. Microscopic examination of the polyimide film using polarized light indicated that the polyimide film was internally stressed in the regions adjacent to each of these stretch defects (Figure 2).

2) Scratch marks at a 60^0 angle with the rolling direction. These scratches were believed to be a result of mechanical processing in the fabrication of the polyimide film (Figure 3).

3) Lumps of polyimide rising out of the surface. A circular stress pattern existed around each of the lumps (Figure 4).

4) Elongated lumps which appeared to be lumps that were pressed out when the material was rolled. They were oriented and had stress patterns parallel to the rolling direction (Figure 2).

5) Holes through the film. Each of these appeared to be a lump defect which had a hole in the middle. Each hole also had a circular stress pattern around it (Figure 5).

Table II

Magnitude and Frequency of Polyimide Defects

Type of Defect	Height	Width	Frequency of Occurrence	Remarks
Stretch Mark	-	-	50 lines/inch	Internal and surface features
Scratch Mark	-	-	100 - 300 lines/inch	On surface at 60% angle to stretch
Elongated Lump	.1 - .3 mil	.1 - .4 mil	4 - 20/inch^2	Aligned with stretch marks
Lump	.1 - .5 mil	1 - 2 mil	4 - 13/inch^2	Random orientation
Lump with hole	$\sim$.5 mil	2 mil, .75 mil hole	.5/inch^2	Random orientation

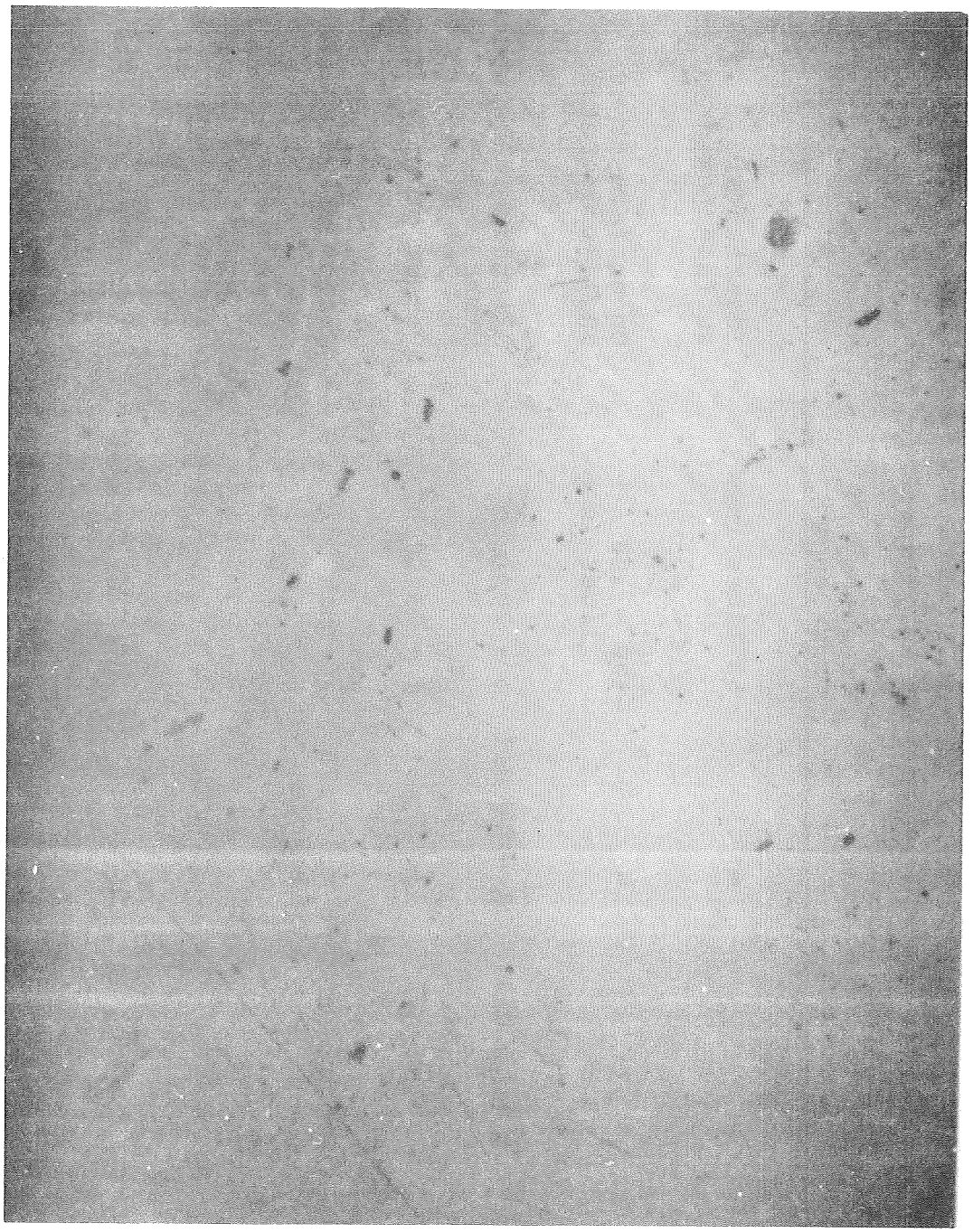


Figure 2. Stretch Marks and Lump in "Kapton" Film. X 65.

Figure 3. Scratch Marks on "Kapton" Film. X 35.

Figure 4. Lump in "Kapton" Film.
X 910.

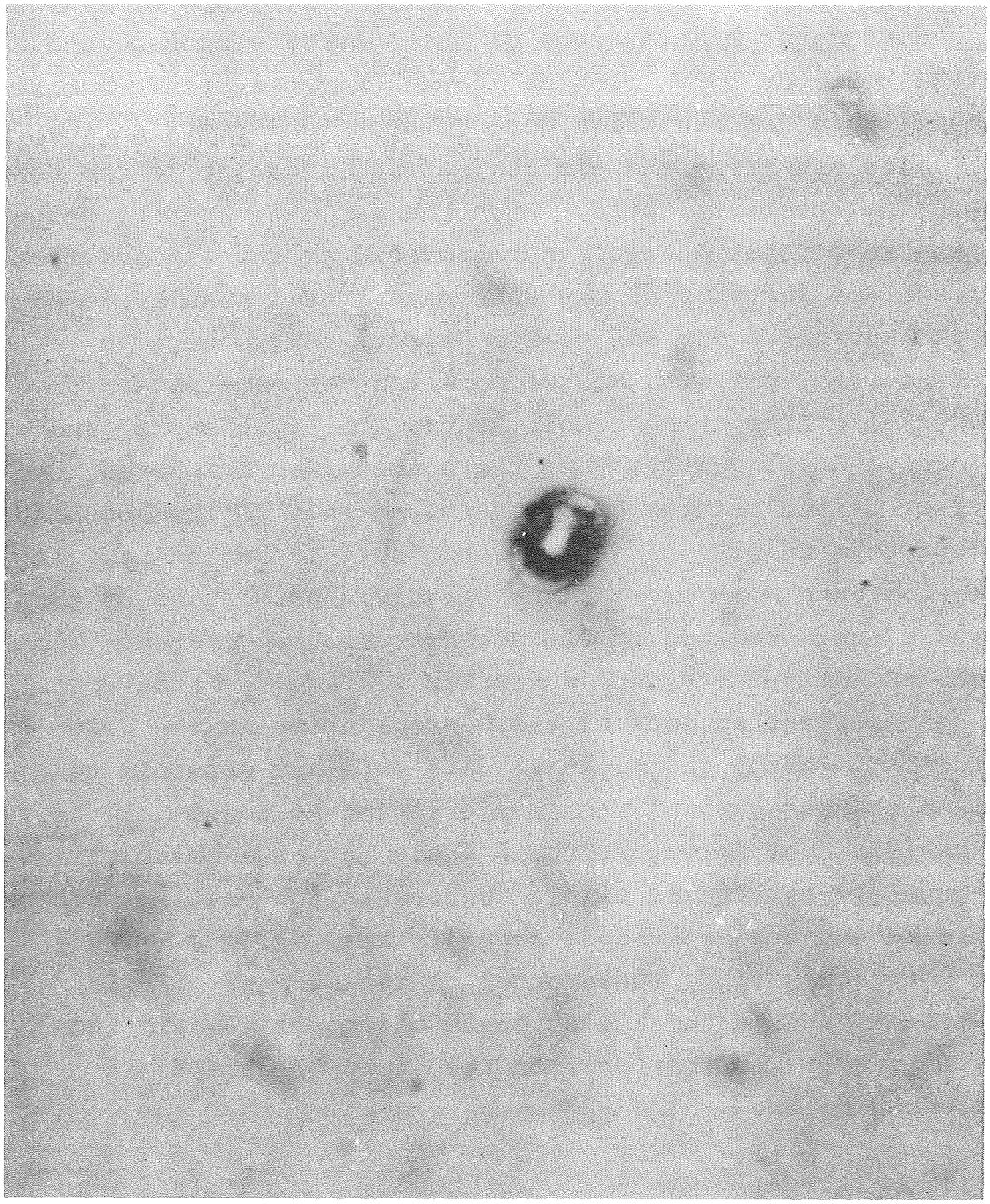


Figure 5. Lump with Hole in Middle in "Kapton" Film. X 965.

Subsequent examinations of the substrate coated with either boron or boron carbide showed that the reinforcement material had defects which were related to defects in the polyimide substrate and also to defects inherent to the reinforcement material itself. When the ceramic vapor condensed on the substrate material it reproduced on its exposed face the surface features of the substrate. As a result, defects in the substrate surface became defects in the ceramic coating. In addition, molten material was sometimes ejected from the ceramic melt to produce "spit marks" and "globs". Consequently, when the coating was completed, the surface of the reinforcement resembled that of the substrate except that it also had "glob" and "spit marks" on it. If the substrate was removed, the freshly exposed face of the ceramic was a replica of the substrate it had coated. The globules, spit marks, and substrate surface features appeared to be important sources of crack propagation in the reinforcement. While quantitative data were not obtained to relate the strength of the reinforcement to these defects, it would be unlikely that there would not be a correlation. In general, relatively simple changes in the coating process could be expected to reduce many of these defects -- they are not necessarily fundamental to the process. It is possible that the tensile strength of the film would then be increased. Further work on the study of defects is presented below.

The Effect of Morphology on Crack Nucleation

A number of boron carbide deposits were prepared and examined in detail to assess the relative importance of the various types of defects found in the condensed boron carbide films. Polyimide substrate specimens were coated with boron carbide on both sides in a special jig which allowed the build up of even coatings on both sides of the substrate. Thin coatings were applied to the polyimide substrate (about 0.05 mil per side) to permit the crack origins to be accurately located in both the substrate and the coating. Figure 6 shows a crack which originated at a spit mark in the coating. Figure 7 shows a crack which originated from a lump defect on the substrate. A tally showed that 60-70% of the cracks were generated by defects such as "globs" or spit marks in the coating. In samples with heavy coatings, many cracks did not have any observable initiation sites. In these cases, cracks appeared to propagate in the reinforcement due to internal stresses produced during the coating process. When samples were strained the majority of new cracks were initiated at residual crack sites.

A tapered bar specimen (see First Year Summary Report)[2] also was examined for crack origins. This specimen consisted of a molybdenum bar which was first coated with Monsanto's Skybond 704 polyimide resin. Boron carbide was then evaporated onto the polyimide surface. This type of polyimide resin had different defects from the DuPont polyimide film but the net result was essentially the same. Approximately 80% of the cracks were started at defects in the boron carbide

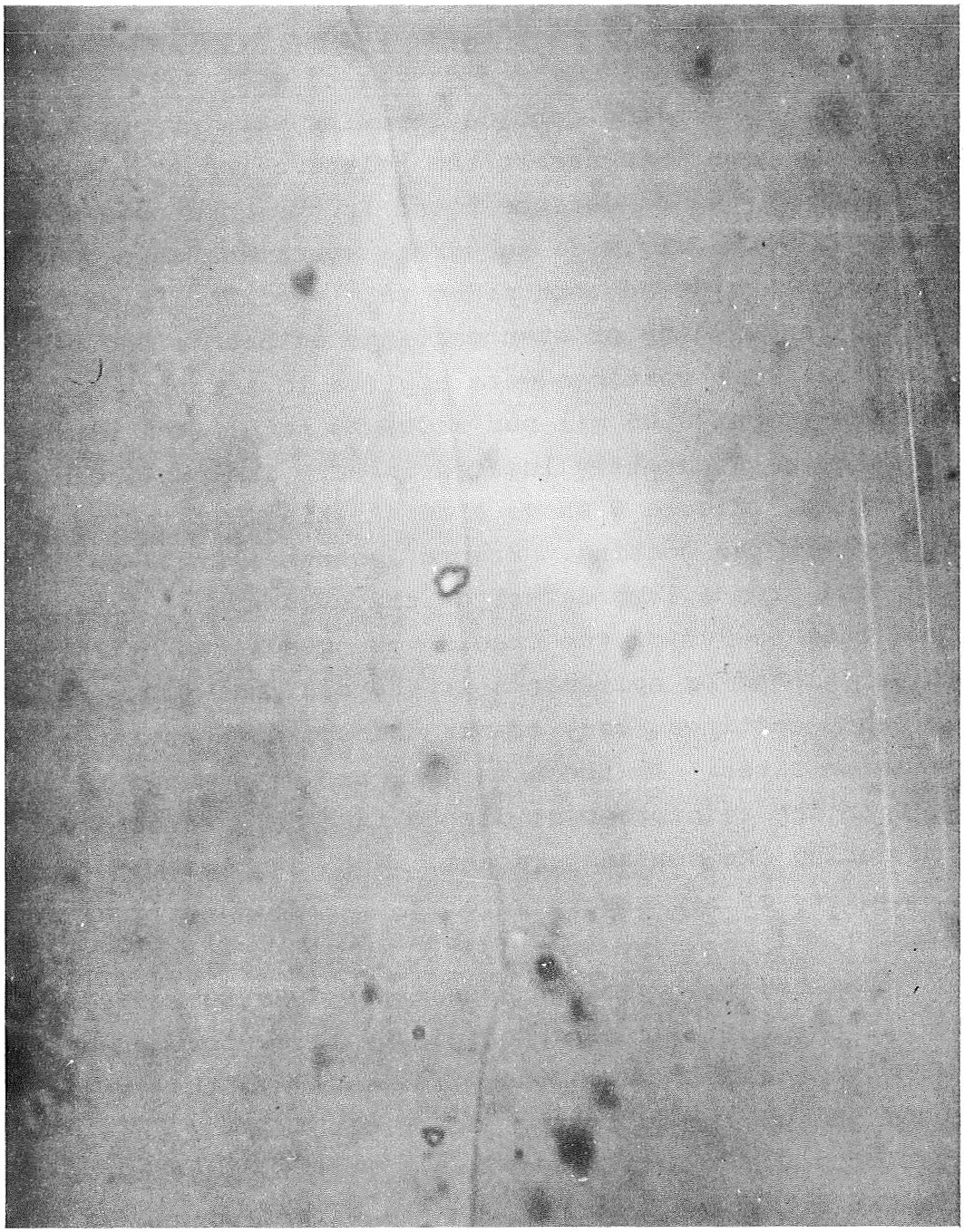


Figure 6. Spit Mark Initiating Crack in Boron Carbide Coating on "Kapton". X 1200.

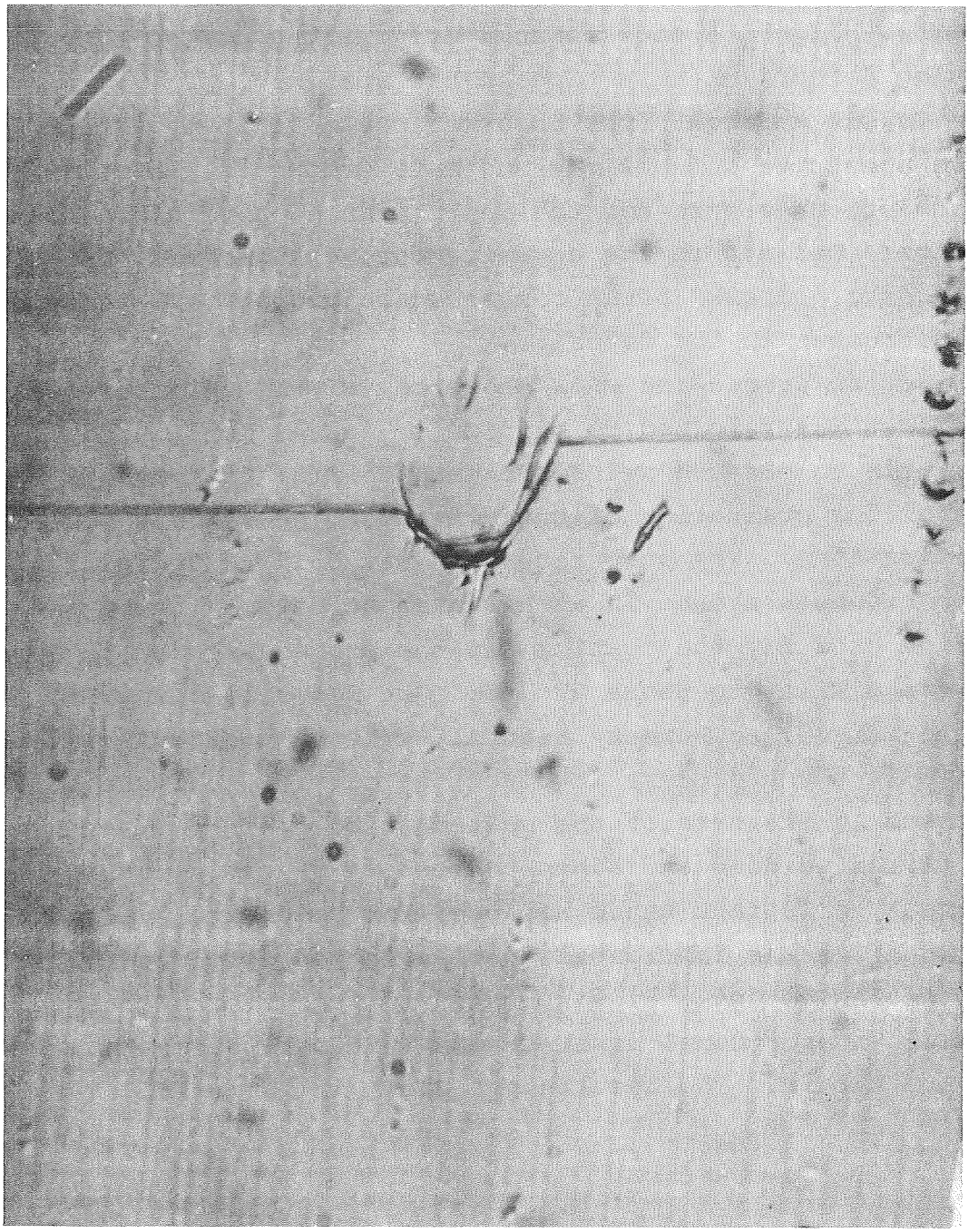


Figure 7. Substrate Defect Initiating Crack in Boron Carbide Coating on "Kapton". X 890.

coating. Figure 8 shows cracks originating at "spit type" coating defects on this tapered bar specimen.

It was apparent from observations of this type that while substrate defects may nucleate cracks in the reinforcement, they were not the major source of reinforcement failure. Defects in the ceramic coating nucleated most of the cracks. Cracks often continued to propogate because of high stresses in the deposits.

Before proceeding with the study of the three process modifications referred to on page 4 it was considered desirable to prepare reinforcement material to serve as a control for evaluation of the effect of the various process modifications. The substrate used was 0.25 mil polyimide which had been stored in an air oven at 65°C. The boron carbide used for the coating and the procedure used to apply it were similar to those used to make material described in the First Year Summary Report.[2] The only significant change in the procedure involved the carrier to increase the macroscopic flatness of the coated film.

After editing and adhesion testing of the control material, a 20 foot batch was used for composite evaluation. The material was fabricated into laminates 121-1 and 121-5. Each of these laminates was tested to measure its elastic modulus, proportional limit stress, ultimate stress and failure strain. The results are shown in Table III.

Figure 8. Spit Mark that Spalled off Tapered Bar Leaving Hole. X 930.

Table III

Mechanical Properties of Process Modification Laminates

Process Modification Represented	Laminate No.	Laminate Size	Number of Layers	Density pci	Vol % Reinforcement	Elastic Modulus 10^6 psi	PL Stress 10^3 psi	Ultimate Tensile Strength
Control	121-1	3/4" x 4"	41	0.0621	44.8	22.1	12.7	22.4
Control	121-5	3/4" x 4"	40	0.0645	44.7	21.5	21.0	27.5
Vacuum Oven Outgas	121-19	3/4" x 4"	35	0.0678	53.4	22.3	15.5	23.6
Vacuum Oven Outgas	121-23	3/4" x 4"	35	0.0604	42.7	20.1	12.7	21.7
High Temp. Deposition on Kapton	121-97	3/4" x 4"	40	0.0608	33.3	15.1	14.3	29.3
High Temp. Deposition on Kapton	121-101	4" x 5"	30	0.0605	34.7	16.5	15.0	30.9
Flatness by Flip-Flop Deposition	121-129	3/4" x 5½"	23	0.0544	22.5	13.5	13.9	13.9
Flatness by Flip-Flop Deposition	121-135	3/4" x 5½"	7	0.0554	23.5	11.8	8.4	15.8

Table III (Cont.)

Mechanical Properties of Process Modification Laminates

Process Modification Represented	Laminate No.	Laminate Size	Number of Layers	Density pci	Vol % Reinforcement	Elastic Modulus 10^6 psi	PL Stress 10^3 psi	Ultimate Tensile Strength
High Temp. Deposition on Aluminum	121-143	3/4" x 4½"	8	--	51.3	28.2	--	36.0
High Temp. Deposition on Aluminum	121-148	3/4" x 5"	10	0.0637	53.6	29.5	19.3	38.2

Vacuum Oven Degassed Material

As outlined in the introduction the main reason for examining the outgassing properties of the polyimide film was to find ways of increasing the degree of adhesion of the boron carbide to the polyimide film. Since the polyimide is formed by a condensation reaction it was considered possible that complete water removal had not been achieved before coating with boron carbide. Consequently, it was possible that after the initial coat of boron carbide, water vapor could accumulate at the polyimide -- boron carbide interface and decrease the adherence. Any plasticizer, solvent or low melecular weight material in the polyimide could act similarly. A degassing step prior to coating, therefore, appeared to be a promising procedure for increasing the boron carbide-polyimide bond.

One pound of 0.25 mil Kapton, specially wound on an aluminum metal core, was obtained from DuPont. This material, on the metal core, was suspended in a vacuum oven so that there was no contact between the polyimide and the oven walls. The oven was evacuated and heated to 110^{0}C. The material was exposed to these conditions for a period of 35 days. An 85 foot length was then loaded into the semi-continuous vacuum coater. Considerable difficulty was experienced during the loading operation. The polyimide film tore very easily. During the coating operation additional difficulty was experienced with tearing of the film. In previous work the polyimide film was given a separate outgassing pass through the vacuum coater prior to coating with boron carbide. This step was not carried out in this case since the polyimide had received the vacuum oven treatment. The film was coated

with boron carbide, edited, and tested for the adherence of the boron carbide to the polyimide substrate. Adhesion was good but was not significantly improved by the more rigorous outgassing. However, the material was flatter and less wrinkled than the control material. This resulted from the reduced amount of handling associated with elimination of the separate outgassing step previously carried out in the vacuum coater. Some of this reinforcement material was fabricated into laminates 121-19 and 121-23. The mechanical properties of these laminates were measured and the results are shown in Table III.

Samples of the polyimide before and after vacuum oven exposure were sent to DuPont for testing. The test results obtained are shown in Table IV with comparative values for the same properties of standard Kapton. It is apparent that both the tensile strength and the elongation values had significantly decreased as a result of the extended vacuum degassing operation.

The significance of these results is considered later under Discussion of Results.

Table IV

Mechanical Properties of "Kapton" Film*

		Typical Values	NRC Sample Before Vacuum Oven Treatment	NRC Sample After Vacuum Oven Treatment
Ultimate Tensile Strength		25,000 psi	23,000 psi	16,000 psi
Ultimate Elongation		70%	70%	8%
Time to 1% Elongation	at 250°C	8 years	-	-
	at 275°C	1 year	-	-
	at 300°C	3 months	-	-
	at 400°C	12 hours	-	-

*Data supplied by DuPont.

High Temperature Deposition of Boron Carbide

The temperature of the substrate during deposition is one of the main variables which would be expected to be related to the strength of the vacuum deposit. In general, highest temperatures commensurate with the stability of the substrate and consistant with low degrees of crystallinity in the deposit would appear to be the most desirable.

Accordingly, two runs were made in which the boron carbide was deposited at temperatures just below that at which obvious thermal degradation of the substrate occurred. In one run the substrate was 0.25 mil polyimide film and in the other the substrate was 2 mil aluminum foil.

Preparation of the polyimide reinforcement material followed the standard procedure except for the deposition temperature. After the coating operation was proceeding normally, the deposition temperature was increased until an "orange peel surface" was seen in the coated material. The temperature was then slowly decreased until these signs of polyimide film degradation just disappeared. The remainder of the film was then coated under these conditions. The resulting boron carbide deposit was bright and shiny and its adhesion to the polyimide substrate was good. This material was fabricated into laminates 121-97 and 121-101 by the procedure detailed in Reference 4 (pp. 17, 18). The laminates were then tested to determine the mechanical properties of the material. The test results are shown in Table III.

Preparation of the aluminum reinforcement material also followed the standard procedure except for the deposition temperature.

In this case, after the coating operation was proceeding normally, the deposition temperature was increased until the foil just began to melt directly over the vapor source. The temperature then was 660°C. The deposition temperature was then reduced just below melting incidence while the boron carbide coating was applied to a 20 foot length of foil. The coating was black, shiny, uncracked, and had very good adherence. Coating thickness was 0.23 ± 0.01 mil. This material was first fabricated into two layer primary laminates which were then assembled into a secondary laminate by substrate removal techniques. To accomplish this, the boron carbide surfaces of paired sheets of reinforcement material were bonded together. The primary laminates thus formed were cut into strips of the proper size for the secondary laminate. These strips were etched in acid to remove the aluminum facing from both sides and were then bonded together by the procedure detailed in Ref. 4, pp. 17, 18. The secondary laminates 121-143 and 121-148 were fabricated in this manner and were tested to determine the mechanical properties of the material. The test results are shown in Table III.

Alternate Two Side Deposition on Kapton

One of the major difficulties in coating polyimide substrates with boron carbide arises because the coefficients of thermal expansion for these two materials are very different. (The coefficient for polyimide film is approximately 40 x $10^{-6}/^{0}C$ while the boron carbide has a coefficient of 3 x $10^{-6}/^{0}C$). Consequently, as a coated substrate cools after coating, the combination curls towards the polyimide. Under these conditions it is very difficult to prevent the boron carbide from being damaged -- and even if not damaged it is difficult to use the direct method of tensile testing to measure either the strength of the coating or the combination. The possibility of progressively building up "sandwich" coatings on both sides of a polyimide substrate and so balancing the stresses arising from differences in the thermal coefficients was the subject considered in this phase of the program. It was really directed to the production of very flat sections of boron carbide-polyimide film. The coating was applied to the polyimide strips with the aid of a so-called "flip-flop" device which was designed to prepare samples for direct testing of single sheets of reinforcement material. This device is described later in this report under the heading: "Tensile Tests of Boron Carbide and Boron on Single Layers of Various Substrates".

Several runs were made with this device to prepare samples of reinforcement material for fabrication of test laminates. For each run, five strips of 0.25 mil polyimide film, 3/4 inch wide by 5½ inches long were mounted in the fixture modules. The chamber was evacuated and the samples were pre-heated to $350^{0}C$. During the coating operation the

temperature of the samples ranged from 350°C to 400°C. While the coating was being applied the fixture modules were turned in a flip-flop mode through a 180° arc to expose the two sides of the Kapton strips alternately to the boron carbide vapor stream. Exposure intervals were five seconds per side and the total coating time during each run was four minutes. The coating rate of about 0.055 mil per minute produced an average coating thickness of 0.11 mil per side. Much of this material was the flattest yet prepared. The samples of reinforcement material were carefully removed from the "flip-flop" modules and coated with a thin layer of epoxy to protect their surfaces. They were then stored in a desiccator until used to prepare the test laminates. A total of 55 samples were made. A set of coated samples after removal from the fixture modules is shown in Figure 9.

The samples were inspected and those with obvious defects, such as spit marks and torn edges were rejected. The remainder were fabricated into laminates 121-129 and 121-135 by the procedure outlined in Reference 4(p. 17). The laminates were tested to determine the mechanical properties of the material. The test results are shown in Table III. The analysis of the results obtained for this alternate two-side coating work is considered in the following Discussion of Results along with the results for the other process modifications described earlier.

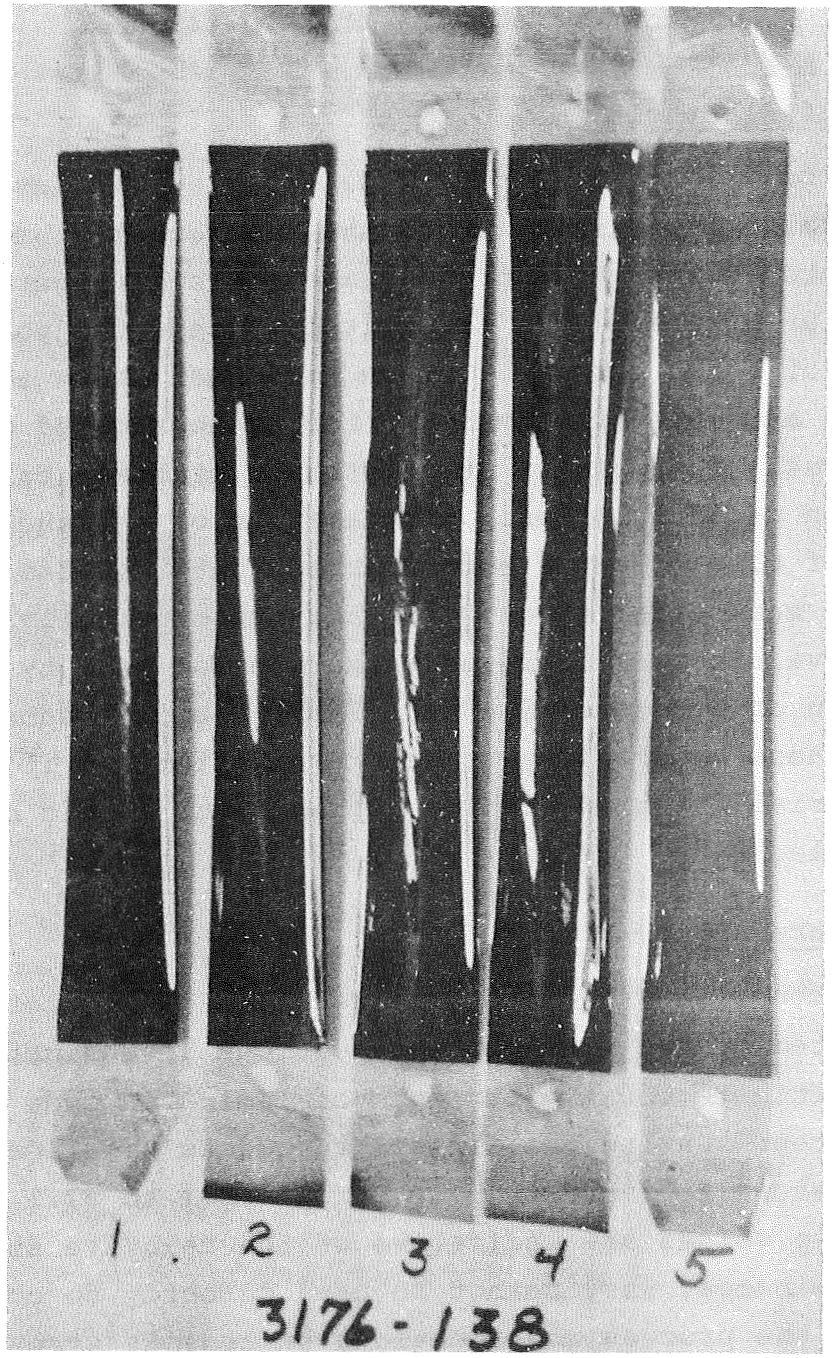


Figure 9. "Kapton" Strips Coated with Boron Carbide in the "Flip-Flop" Fixture. X 0.70.

Discussion of Results

Modulus of Elasticity

The relationships between the measured modulus and the boron carbide concentration for the reinforcement modifications investigated during this program are shown in Figure 10 where the modulus of elasticity is plotted against the volume fraction of boron carbide. Lines have been drawn to indicate 60%, 80%, and 100% translation effectiveness based on the Rule of Mixtures. The modulus of elasticity of boron carbide has been taken as 60×10^6 psi. Translation of the theoretical modulus of elasticity of boron carbide into all laminate specimens was better than 70% of that theoretically attainable. The best values were achieved with material made by alternate deposition or by deposition on a 2 mil aluminum substrate. Both of these materials were relatively flat and it is apparent that material for high modulus applications should be as flat as possible.

Tensile Strength

The tensile strength of the reinforcement material was affected by the process modifications investigated. The average ultimate tensile strength of laminates made from material representing the different process modifications has been shown to range from 14.9×10^3 psi to 37.1×10^3 psi. While these values are indicative of the relative strengths of the laminates, they cannot be used directly to compare the effect of the process modifications on tensile strength because there are different percentages of ceramic coating, polyimide and glue in each laminate as shown in Table V. These materials all have different tensile strengths.

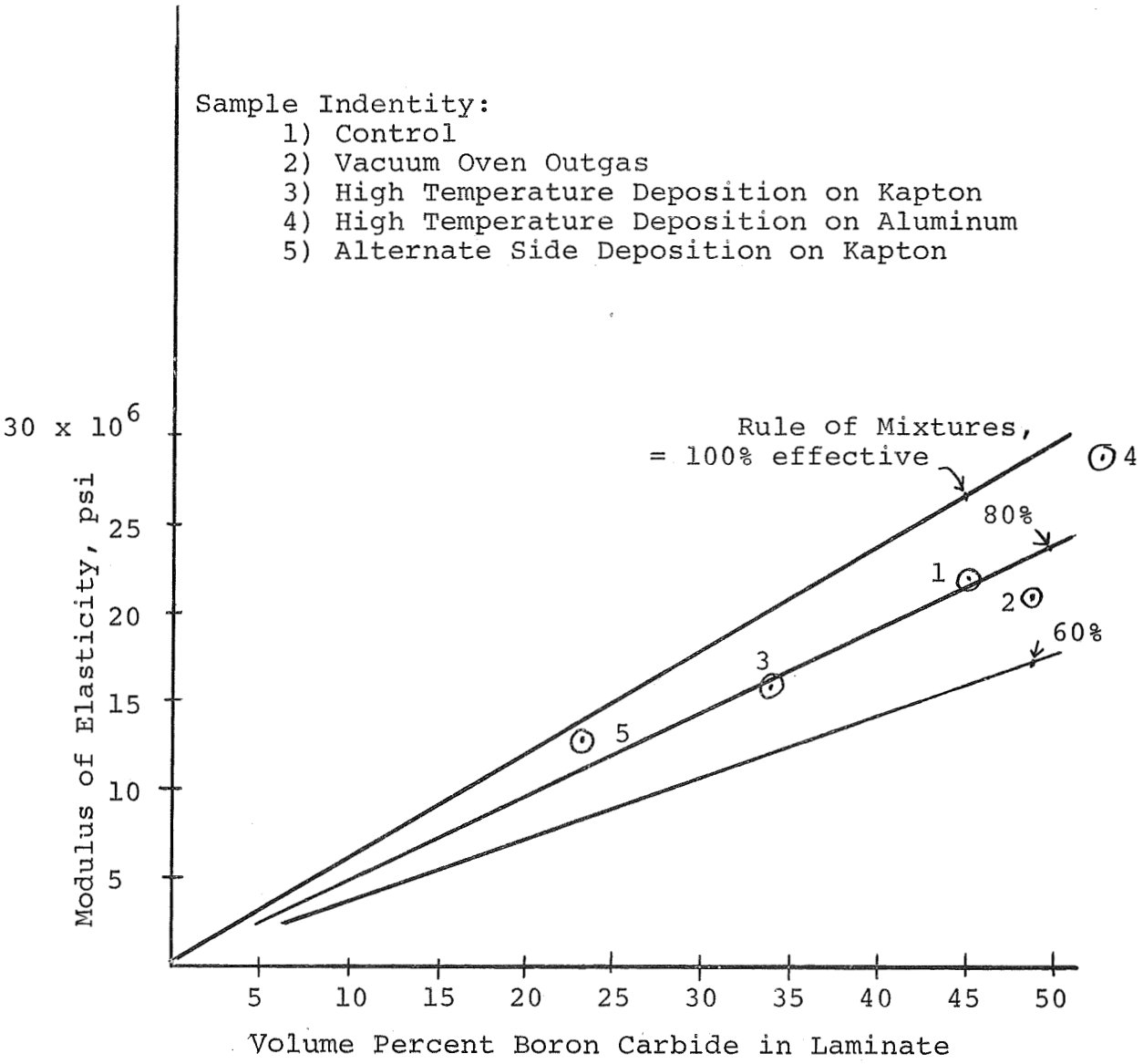


Figure 10. The Elastic Modulus of Reinforcement Laminate Specimens as a Function of the Volume Fraction of Boron Carbide.

Table V

Composition of Process Modification Laminates

Process Modification Represented	Laminate No.	Total Thickness mils	Polyimide Film Thickness mils	B_4C Thickness mils	Volume Percent B_4C	Volume Percent Polyimide	Volume Percent Epoxy	Tensile Strength at 0% B_4C
Control	121-1	27.48	11.1	--	44.8	40.4	14.8	
	121-5	27.13	10.8	--	44.7	40.6	14.7	
Average Values					44.75	40.5	14.7	20.4
Vacuum Oven Outgas	121-19	19.66	8.05	--	53.4	40.9	5.7	
	121-23	23.70	8.05	--	42.7	34.0	23.3	
Average Values					48.05	37.45	14.5	13.7
High Temperature Deposition on Kapton	121-97	22.50	12.80	--	33.3	56.8	9.9	
	121-101	16.55	9.60	--	34.7	58.0	7.3	
Average Values					34.0	57.4	8.6	22.7
Flatness by "Flip-Flop" Deposition	121-129	23.08	6.9	5.2	22.5	29.9	47.6	
	121-135	6.55	2.24	1.54	23.5	34.2	42.3	
Average Values					23.0	32.05	44.95	15.1
High Temperature Deposition on Aluminum	121-143		--	--	51.3	--	48.7	
	121-148		--	--	53.6	--	46.4	
Average Values					52.45	--	47.55	8.0

A comparison may be made by plotting the ultimate tensile strengths of all laminates against the volume fraction of contained boron carbide. Such a plot is shown in Figure 11. The lines representing the effect of each process modification have been drawn through two points. One point is the average of the tensile strength values determined for the two laminates representing each process modification. (See Table III) The second point is the calculated tensile strength of a composite containing the same proportions of polyimide and glue but no boron carbide. The calculated values for zero percent boron carbide are shown in Table V. The tensile strength values used in these calculations were determined on samples of the material being used. The values used for polyimide film were determined by the manufacturer to be 25×10^3 psi for as received material and 16×10^3 psi for the vacuum oven outgassed material. The value used for the epoxy glue was determined by testing tensile specimens cast from a standard mix used to fabricate laminar composites. The measured value was 8×10^3 psi.

The plots in Figure 11 indicate that material prepared by the high temperature deposition of boron carbide produced the strongest laminates. At a boron carbide concentration of 40%, for example, both sets of high temperature laminates show a tensile strength of about 30×10^3 psi. At this reinforcement concentration the control laminates showed a strength of about 25×10^3 psi and the vacuum oven outgassed laminates about 21×10^3 psi. The laminate prepared from alternate two side deposition material shows no relation at all between strength and boron carbide concentration. Examination of the ruptured specimens showed they had failed

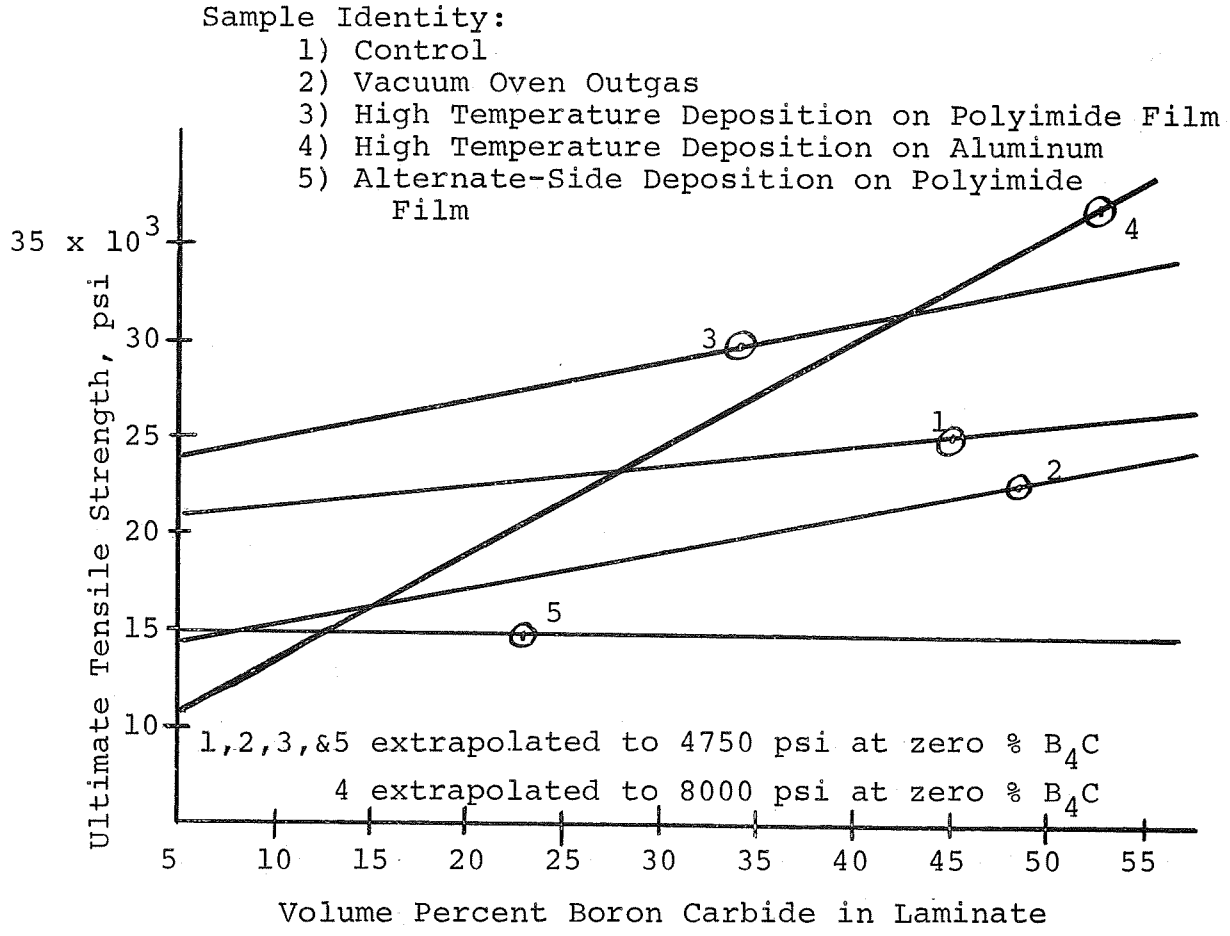


Figure 11. Ultimate Tensile Strength of Reinforcement Laminate Specimens as a Function of the Volume Fraction of Boron Carbide.

prematurely because of poor adhesion of the boron carbide to the polyimide film. As a result of this poor adhesion the boron carbide did not contribute to the strength of the laminate and it was not possible to determine the effect of the flatness of the material on the tensile strength of the reinforcement. The tensile strength value measured for these "flip-flop" laminates resulted from the combined contribution of the strength of the polyimide film and the epoxy adhesive. The boron carbide appeared to make no contribution at all. The horizontal plot for this reinforcement as a function of concentration is consistant with the fact that the boron carbide had failed in tension and was not bonded to the polyimide film.

The strength of the boron carbide alone may be estimated using the data presented in Tables III, IV, and V, and the Rule of Mixtures. While this procedure has severe limitations it may be used as a guide to indicate the relative effect of the various process modifications considered. In calculating the strength of the boron carbide film the effective strengths of the other materials which were in the laminates actually tested were taken to be:

Polyimide Film (Control)	25×10^3 psi
Polyimide Film (Vacuum Degassed)	16×10^3 psi
Epoxy Resin	8×10^3 psi

The results of these calculations are presented in Table VI.

Vacuum oven outgassing of the polyimide substrate produced no significant change in the estimated strength of the

Table VI

Estimated Values of the Strength of Boron Carbide Film in Various Process Modification Laminates

Modification	Calculated Strength of Boron Carbide
Control	30.2×10^3 psi
Vacuum Oven Outgas	31.7×10^3 psi
High Temperature Deposition on Polyimide	44.2×10^3 psi
Alternate Deposition	14.5×10^3 psi*
High Temperature Deposition on Aluminum	63.5×10^3 psi

*Poor Adhesion

boron carbide. The values of 30.2×10^3 psi for the control material and 31.7×10^3 psi for the outgassed material are not significantly different. The difference in strength of the laminates representing these two materials, as shown in Figure 11, was probably dependent on the reduced strength of the vacuum oven outgassed polyimide film.

Deposition at higher temperatures appeared to improve the strength of the boron carbide coating. The value of 44.2×10^3 psi for the strength of the coating deposited on polyimide film was almost 50% greater than the value of 30.2×10^3 psi for the coating on the control material. The temperature at which the coatings were deposited in the two cases was not measured directly. However, approximate temperatures could be inferred from related data. Calculations from measurements of the curvature of deposited coatings and known coefficients of expansion of boron carbide and polyimide indicated that normal deposition temperatures range between 250°C and 300°C. The weight loss study showed that the polyimide film could withstand temperatures up to 450°C in vacuum without serious decomposition. Previous work had shown that at temperatures between 500°C and 550°C in vacuum the decomposition of polyimide film was serious enough to produce a poor coating and to weaken the polyimide so that extensive rupturing of the film occurred. During the high temperature deposition, the operating conditions were adjusted to obtain as high a deposition temperature as possible without producing either a high chamber pressure or an extensive rupturing of the polyimide film. The deposition temperature was estimated to have been in the range 400°C to 450°C.

During the formation of the boron carbide coating on aluminum the deposition temperature was higher. In this case the energy input to the aluminum substrate was increased during deposition of the coating until the aluminum just began to melt when directly over the source. The energy input was then decreased slightly to just prevent melting. The coating was deposited under these conditions. Since the melting point of aluminum is $660^{0}C$, the deposition temperature was estimated to range from $550^{0}C$ to $600^{0}C$. The ultimate tensile strength calculated for the boron carbide coating deposited on aluminum at this higher temperature was 63.5×10^{3} psi. This was the strongest coating produced by any of the process modifications in the present program.

THE STRENGTH OF INDIVIDUAL FILMS

One of the major difficulties in the past work on the structural properties of thin ceramic films has been that there has not been a satisfactory solution to the problem of how to measure the strength of these films. Internal stresses in the films have caused the films to bend and break when removed from the substrates. Thermal expansion differences between the films and substrates have resulted in curling and bending stresses. A number of other difficulties rise. Test specimens cut from larger sheets of material may fail prematurely and yield low strength values because the cutting initiates edge cracks which extend rapidly under stress. Test specimens prepared from laminates which have been fabricated from several sheets of film are less susceptible to this edge effect but introduce errors related to dilution of the reinforcement content by the adhesive which bonds the laminate layers together. In addition the films may be degraded by the handling and pressing required during the laminating process. Test specimens prepared by deposition of a ceramic coating onto a tapered metal bar (see First Year Summary Report)[2] gave ambiguous results because of thermal pre-strains introduced by thermal expansion coefficient mismatches. There has not been a convincing procedure for measuring the strength of the boron, boron carbide coatings, consequently, other methods were sought. These included testing of individual films obtained by separating flakes of coatings from the substrates on which they were deposited after taking special precautions to reduce the curling stresses. Work was also

initiated on the deposition of boron and boron carbide onto thin metallic substrates where the thermal expansion differences would be small.

In the course of the work it became apparent that additional problems were being introduced by possible variations in the boron-carbon ratio in the films formed on the evaporation of boron carbide. Accordingly, this part of the program began to give more detailed attention to the boron system. It was considered that it would probably be possible to directly relate the information gained on boron to boron carbide at a later date.

The description of the work carried out has been divided into two main parts. Firstly, a description of the work on the direct testing of boron carbide flakes, and secondly, a description of the more extensive work associated with the deposition of boron carbide on polyimide film and boron on titanium, tungsten and tantalum. Each of the latter were tested without separation from the substrates.

Tensile Testing of Boron Carbide Flakes

Free flakes of boron carbide were obtained from samples of reinforcement material which had been prepared in the semi-continuous coater using two different substrates. The first substrate (Run 42-270) was 2 mil aluminum foil and the second (Run 42-272) was 0.5 mil titanium foil. Specimens of boron carbide flakes were removed from these substrates by short exposure to etchants or by thermal shock. Selected specimens were mounted in a testing jig for determination of their tensile strength. The testing jig, shown in Figure 12, permitted horizontal mounting of the flake so that the gripping adhesive (diphenyl carbazide) could be melted in place and the test begun immediately without further handling of the samples. The test results are listed in Table VII. The highest strength measured was 131 x 10^3 psi. The mean value was 64 x 10^3 psi for the thinner set of flakes and 40 x 10^3 psi for the thicker set.

This procedure required careful experimental procedures but it was direct and gave credible results for the flakes as mounted. However, there was a question as to whether the samples were affected by the procedures for removing them from the substrate. There was some evidence that the boron carbide was attacked by the acid etchant mix used to dissolve the titanium.

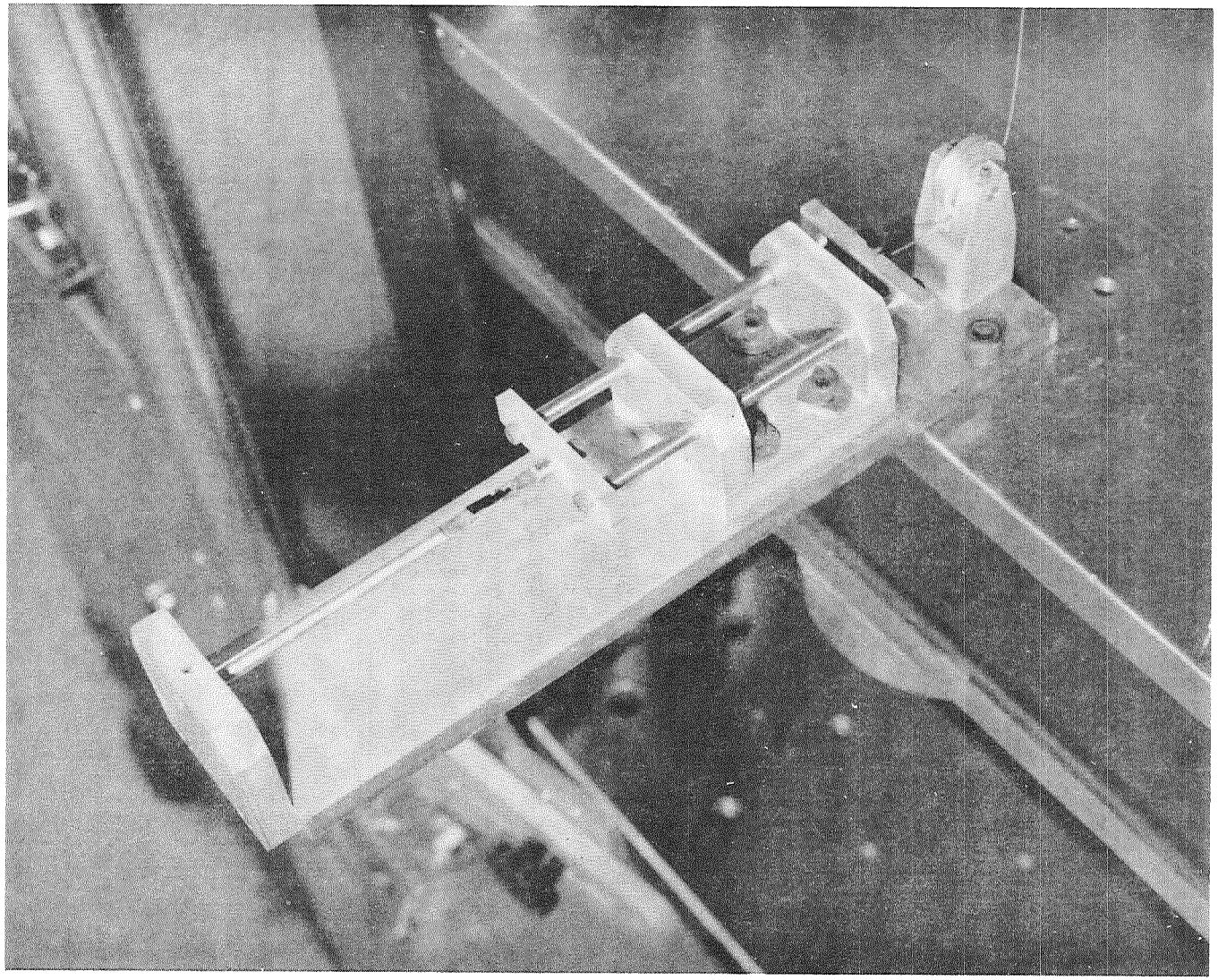


Figure 12. Jig Used to Test Free Flakes of Ceramic Films. X 0.30.

Table VII

The Strength of Boron Carbide Reinforcement Films
(Tensile Test of Free Flakes)

Spec. No.	Coating Thickness 10^{-3} in.	Tensile Strength psi
42-272-1	1.03	44,300
-2	1.07	45,700
-3	0.90	54,500
-4	0.78	44,600
-5	0.90	40,500
-6	1.33	30,900
-7	1.30	43,000
-8	0.72	54,500
-9	1.43	20,000
-10	1.57	25,500
Average		40,350
42-270-1	0.18	40,000
-2	0.18	83,600
-3	0.18	28,000
-4	0.18	86,800
-5	0.18	68,700
-6	0.18	30,700
-7	0.18	43,400
-8	0.18	131,000
Average		64,025

Tensile Tests of Boron Carbide and Boron on Single Layers of Various Substrates

As outlined earlier, previous attempts to prepare single sheet samples of reinforcement material by deposition of a ceramic coating onto a polyimide film or metal foil substrate pre-cut to test size were not successful. Stresses in the coating itself and between the coating and the substrate caused the reinforcement to curl during application of the first side coating and this curl could not be reversed during application of the second side coat. Samples flat enough for tensile testing could not be prepared in this manner.

The concept of coating a pre-cut test sample with a number of thin layers applied alternately to the two sides was tried and found to be quite promising. A simple "flip-flop" fixture was constructed to permit samples to be coated in this manner. The fixture is shown in Figure 13. In use, narrow strips of polyimide or metal were mounted in the module and then flipped back and forth, alternately exposing both sides of the substrate to the vapor source. The flipping was programmed to produce short equal exposures of the two sides of the substrate, repetitively, for as long an interval as desired. Initial tests showed that this technique could produce two-side coated strips of reinforcement material flat enough for tensile testing. The first test samples were prepared by depositing boron carbide on 0.25 mil polyimide film. The samples had two main types of defect: cracks in the coating traversing the width of the specimens, and shallow waves extending the length. These samples were not tested. They showed, however, that the concept was feasible.

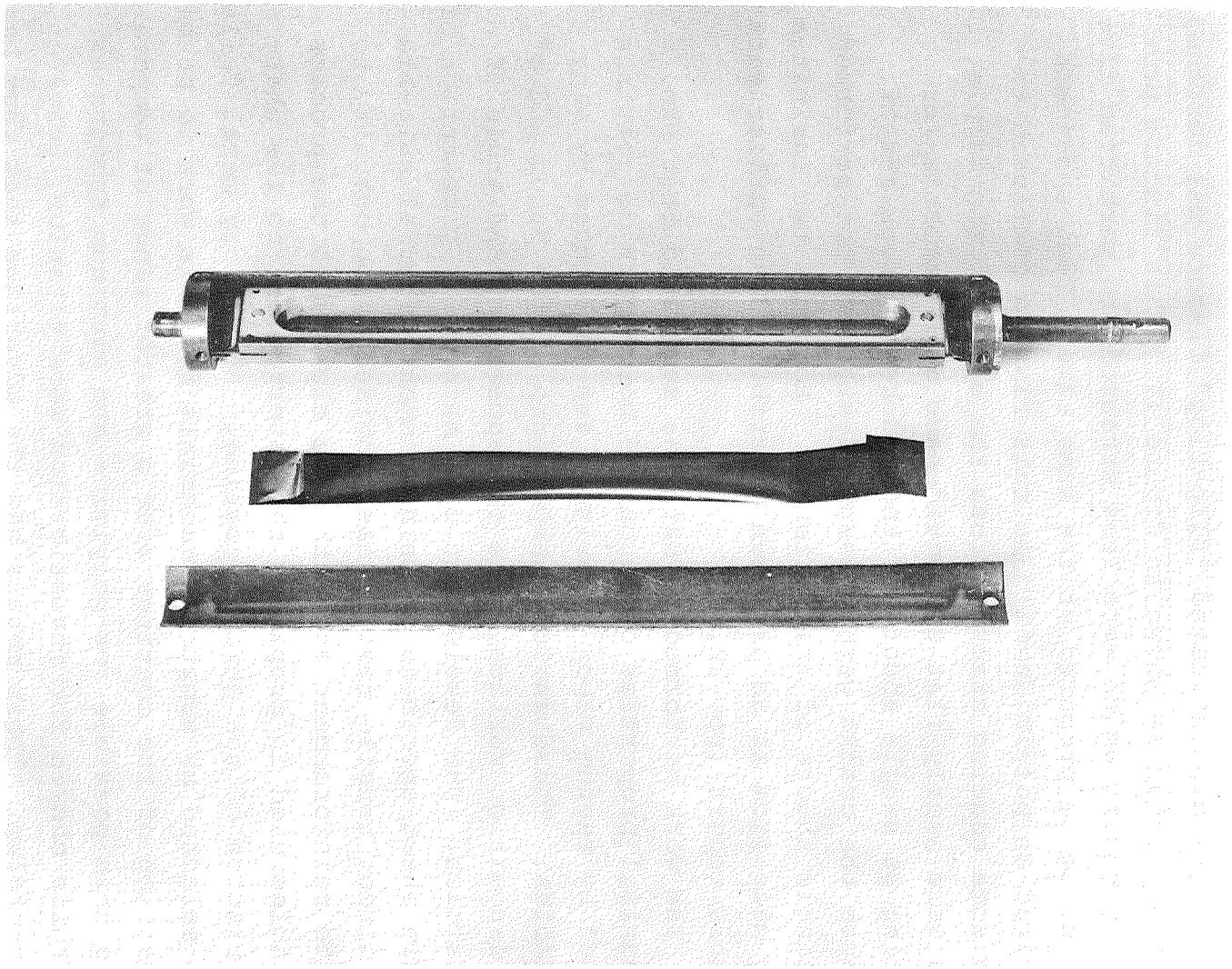


Figure 13. Single Module "Flip-Flop" Fixture. X 0.45.

A more sophisticated "flip-flop" fixture was designed and constructed as shown in Figure 14. This fixture produced deposits which were less stressed and permitted five samples to be prepared at the same time. Test specimens prepared on polyimide film in this fixture continued to show some coating cracks across the width of the sample. Many were nearly flat and would have been suitable for testing as single sheets if the cracks had been absent. Because the cracks were present, tests were not performed on single sheets of this material. However, two laminates were made from it as has been described in an earlier part of this report (pp. 29,30).

The work performed to date has suggested that the mechanical properties of boron and boron carbide coatings formed by vacuum vapor deposition are influenced by many variables. These include temperature of the vapor and of the deposition surface, rate of deposition, and angle of deposition. The development of a method for preparation of single sheet specimens of reinforcement material suitable for direct tensile testing has provided an opportunity to relate reinforcement strength more closely to the process variables used in preparing the material and to the characteristics of the ceramic coating. Refractory metal foils were selected as substrate materials for this work to permit deposition of the coatings over a greater range of temperatures than possible for polyimide and aluminum substrates. The foils chosen for investigation were titanium, tungsten, and tantalum. These metals had the advantage that they have relatively low coefficients of thermal expansion -- values which are close to those of boron and boron carbide.

The work carried on in the program for each of these materials is described below.

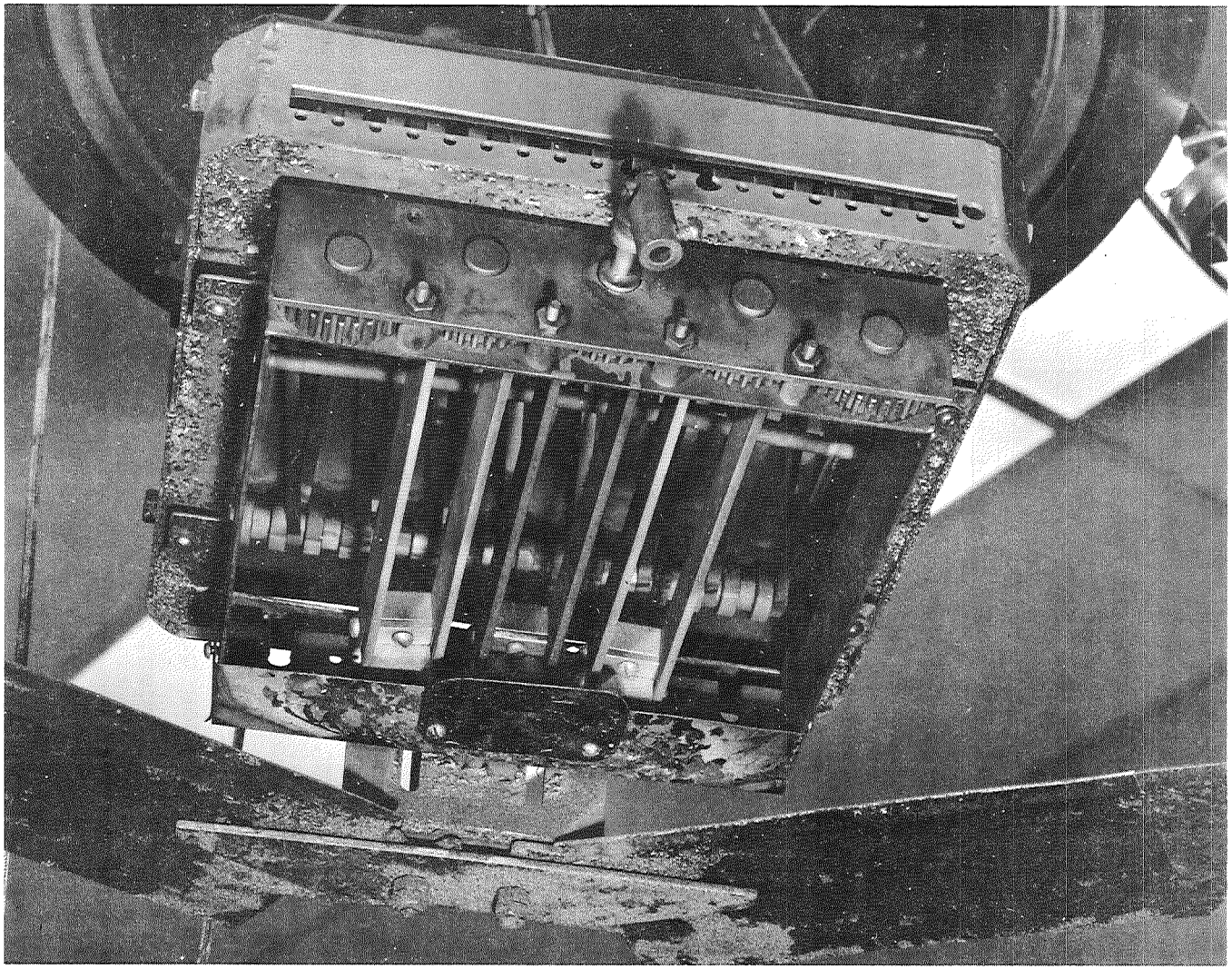


Figure 14. Five Module "Flip-Flop" Fixture. X 0.35.

Preparation and Testing of Boron-Titanium Specimens

The first part of the work with titanium aimed at preparing relatively standardized substrate materials with known mechanical properties. Samples of titanium were pretreated using conditions which would simulate those encountered during the coating process. It was considered that a comparison of the mechanical properties of both the coated and uncoated substrates would yield detailed information of the mechanical properties of the coating.

Accordingly, a length of 0.5 mil titanium foil was annealed in a vacuum furnace at a temperature of 600°C. Five coupons 0.75 inch wide by 6.25 inches long were cut from this material. These coupons were solvent cleaned and chemically polished. They were then mounted in the "flip-flop" fixture in the same manner as they would be if they were to be coated. The chamber was evacuated to a pressure of 1×10^{-5} torr and the coupons exposed to two heating periods while being flipped back and forth. During the first heating period the temperature was held at 600°C. The temperature was then reduced to 550°C for the second heating period and was held at this value to simulate the temperature exposure during the coating operation. The coupons were then cooled, removed from the vacuum chamber, and cut into two pieces, each 0.75 inch by 3.1 inches. Strain gauges were mounted on one half of each coupon so that a stress-strain curve could be obtained and both halves were then tested in tension. The stress-strain curves are shown in Figures 15 and 16. The test data and tensile strengths calculated for the uncoated titanium specimens are shown in

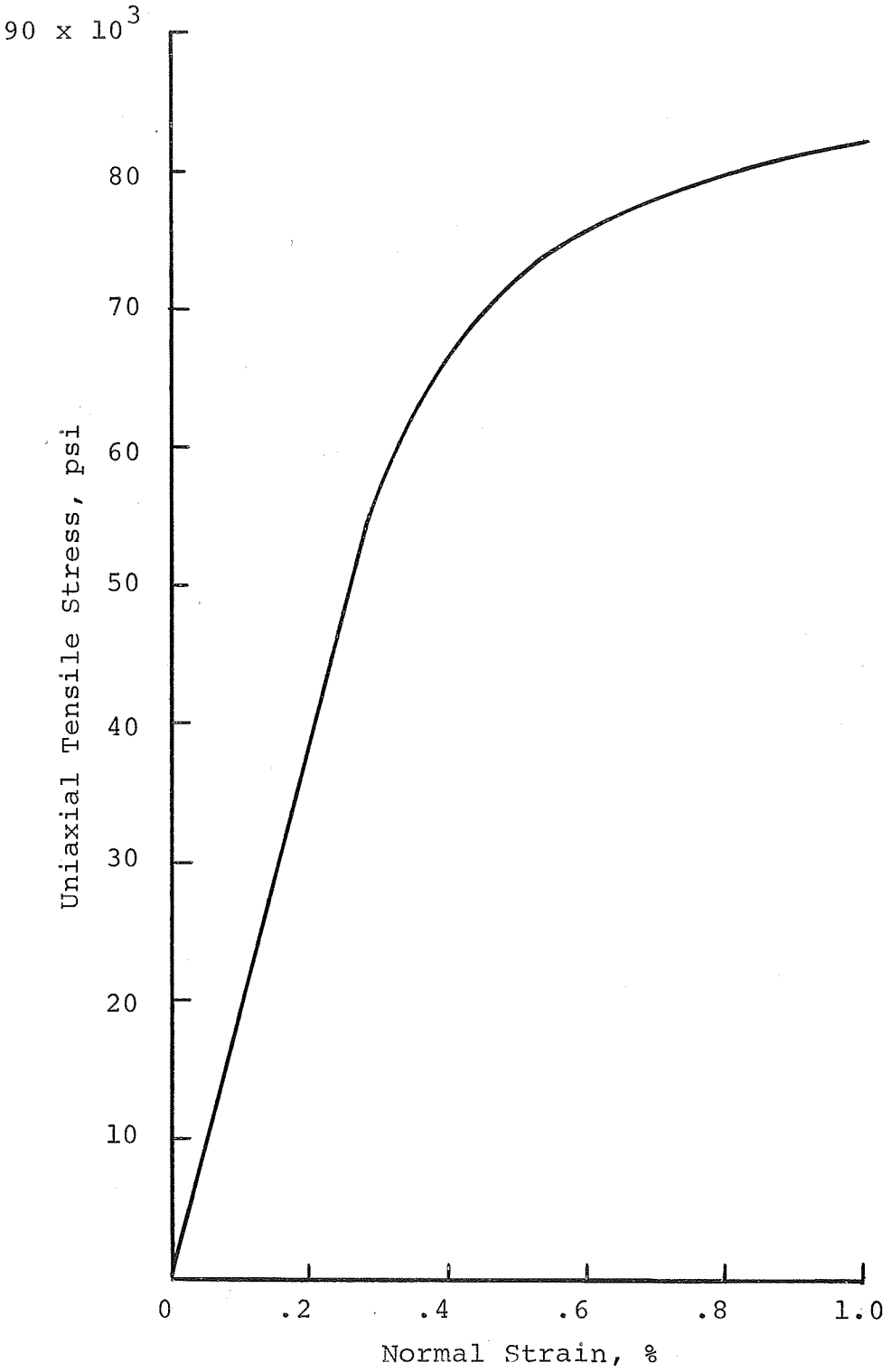


Figure 15. Stress-Strain Curve for Specimen 163-1A, Annealed Titanium.

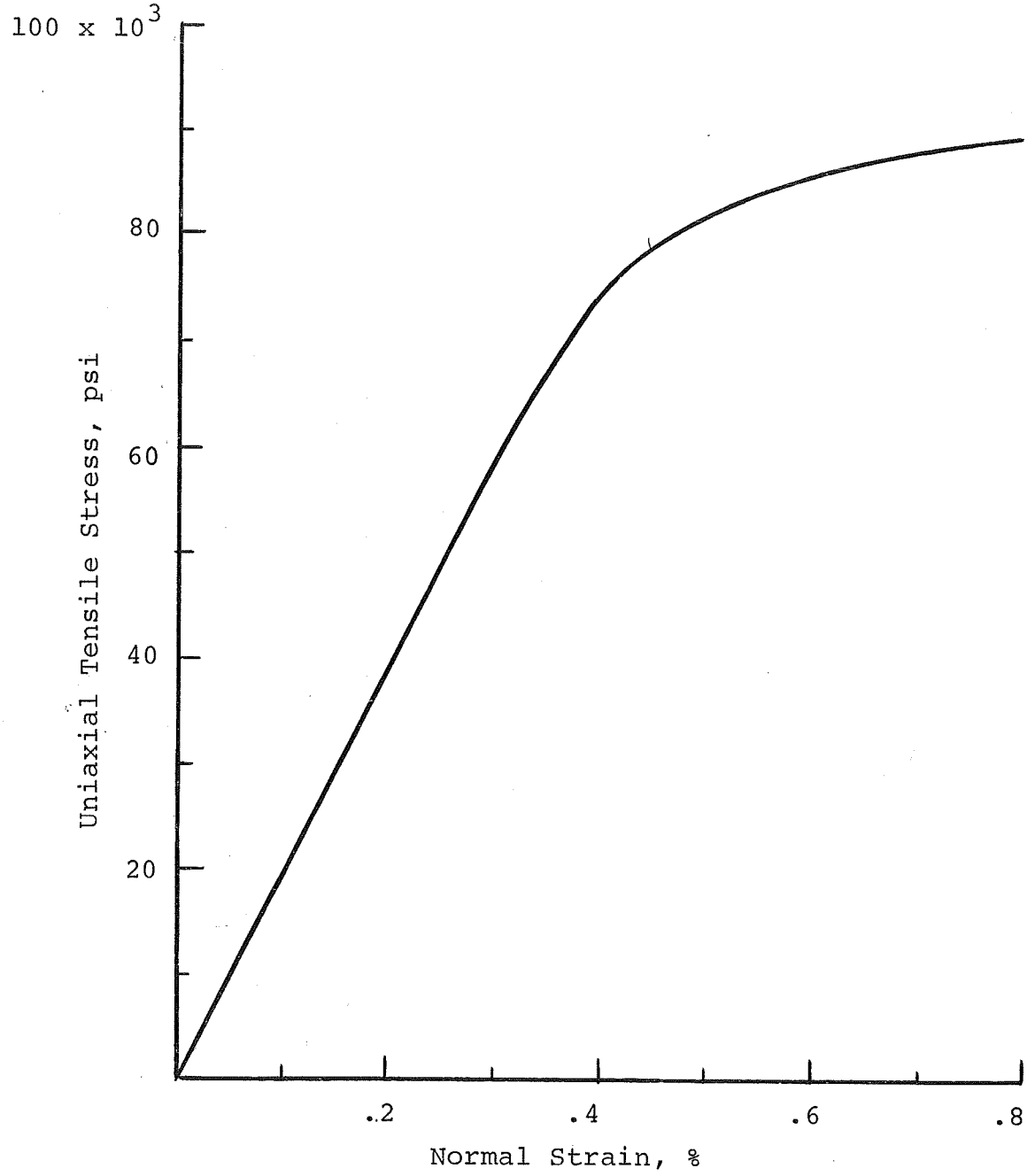


Figure 16. Stress-Strain Curve for Specimen 163-2A, Annealed Titanium.

Table VIII. The average tensile strength was 85.7 x 10^3 psi.

To prepare a typical set of coated test specimens, five strips of titanium foil were solvent cleaned and chemically polished. They then were mounted in the modules in the "flip-flop" fixture and the coating chamber was evacuated to a pressure of 1 x 10^{-5} torr. The strips were heated to 600°C for 30 minutes and then were allowed to cool to 530°C prior to the coating operation. The boron coating was applied while the modules holding the samples were rotated back and forth through a 180° arc around their lengthwise axes. This rotation flipped the samples over, alternately exposing their two sides to the depositing ceramic vapor. Each exposure interval lasted five seconds, minus the fraction of a second required for flipping. After vapor deposition was completed, the specimens were cooled to room temperature in vacuum before they were removed from the coating chamber. Two sets of coated specimens were made to determine the effect of coating thickness. In one set, the total coating thickness averaged 0.65 mil or 0.325 mil per side. Four of these samples were suitable for testing. In the second set, total coating thickness averaged 0.24 mil or 0.12 mil per side. Two of these samples were suitable for testing. The samples were cut in half to produce two test specimens from each sample. Strain gauges were mounted on one specimen from each sample and then all specimens were tested in tension. The stress-strain curves are shown in Figures 17 through 23. The test data and tensile strengths calculated for the boron coated titanium specimens are shown in Table IX.

Table VIII

Tensile Strength of Uncoated Titanium Foil Coupons

Coupon No.	Thickness mil	Load Area Sq. inches	Fracture Force pounds	Tensile Strength 10^3 psi
163-1A	0.39	0.293	24.0	82.1
163-1B	0.39	0.293	22.4	76.6
163-2A	0.32	0.240	21.9	91.2
163-2B	0.32	0.240	21.9	91.2
163-3A	0.30	0.226	20.0	88.9
163-3B	0.30	0.226	20.0	88.9
163-4A	0.42	0.315	28.9	91.8
163-4B	0.42	0.315	28.7	91.2
163-5A	0.30	0.226	18.9	84.0
163-5B	0.30	0.226	16.1	71.5

Average 85.7 ± 10

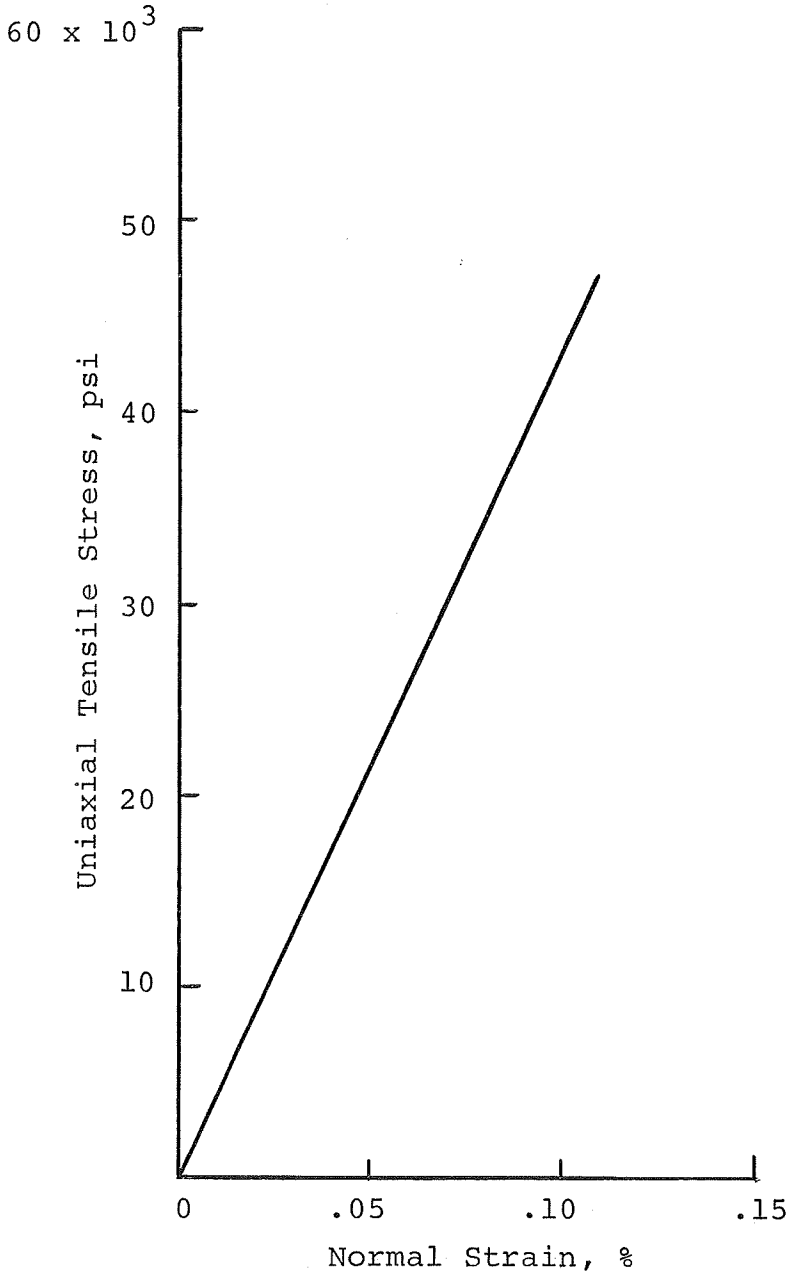


Figure 17. Stress-Strain Curve for Specimen 161-1A, Boron-Titanium.

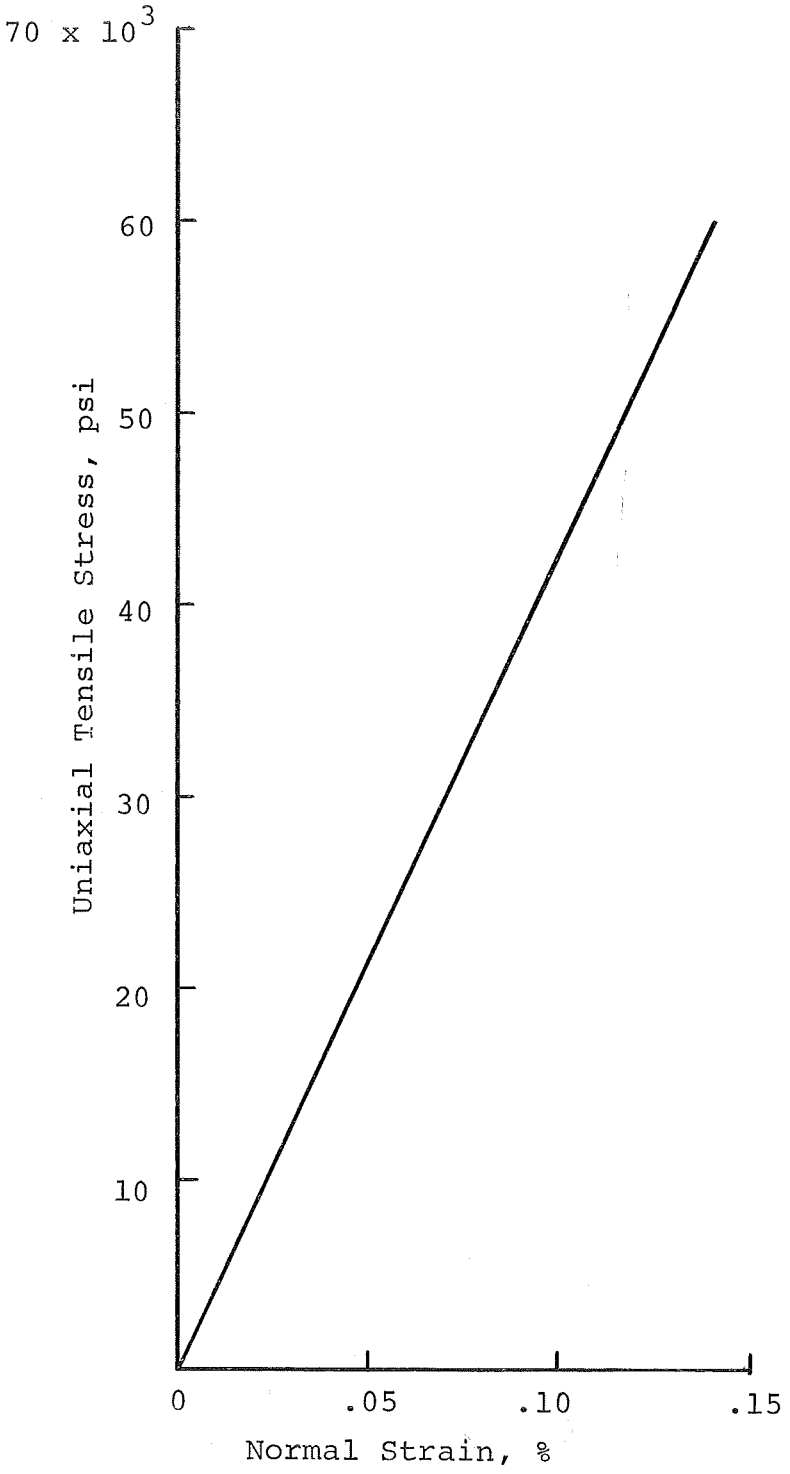


Figure 18. Stress-Strain Curve for Specimen 161-2A, Boron-Titanium.

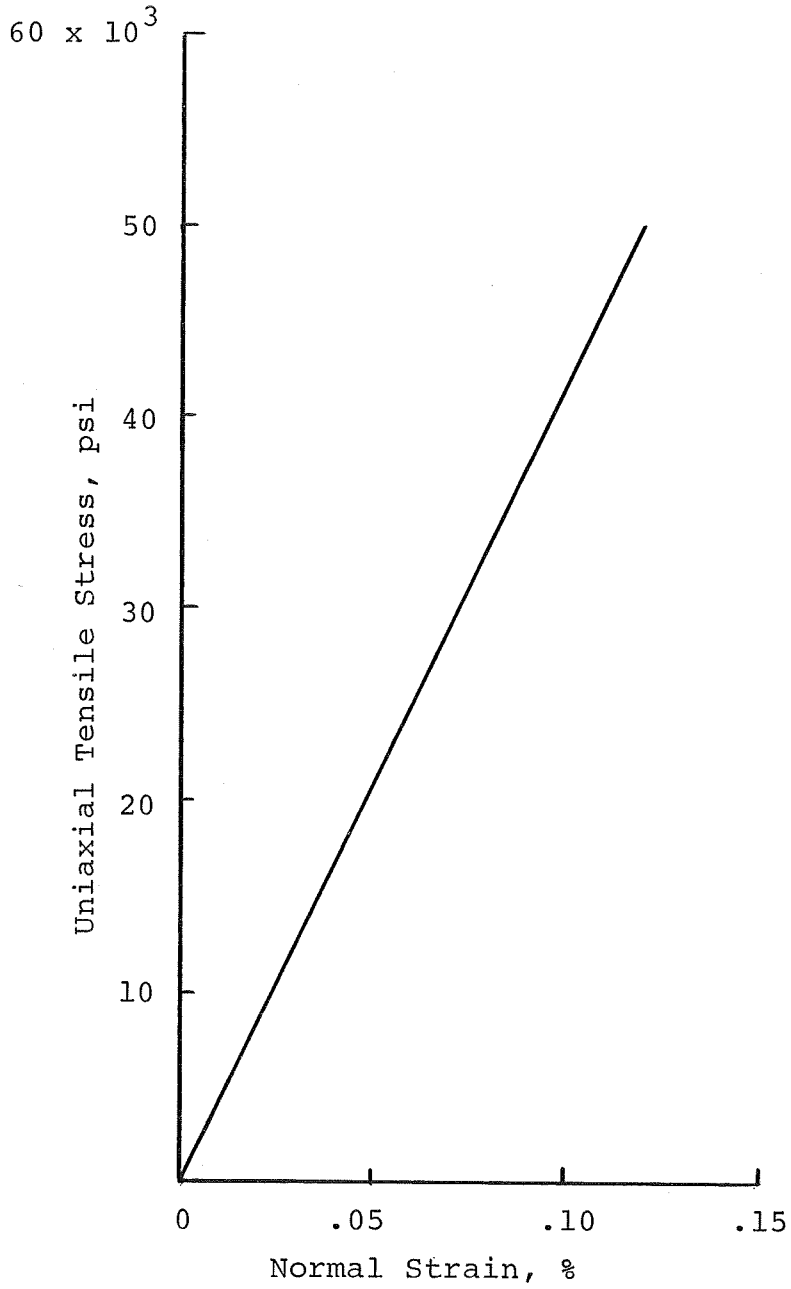


Figure 19. Stress-Strain Curve for Specimen 161-3A, Boron-Titanium.

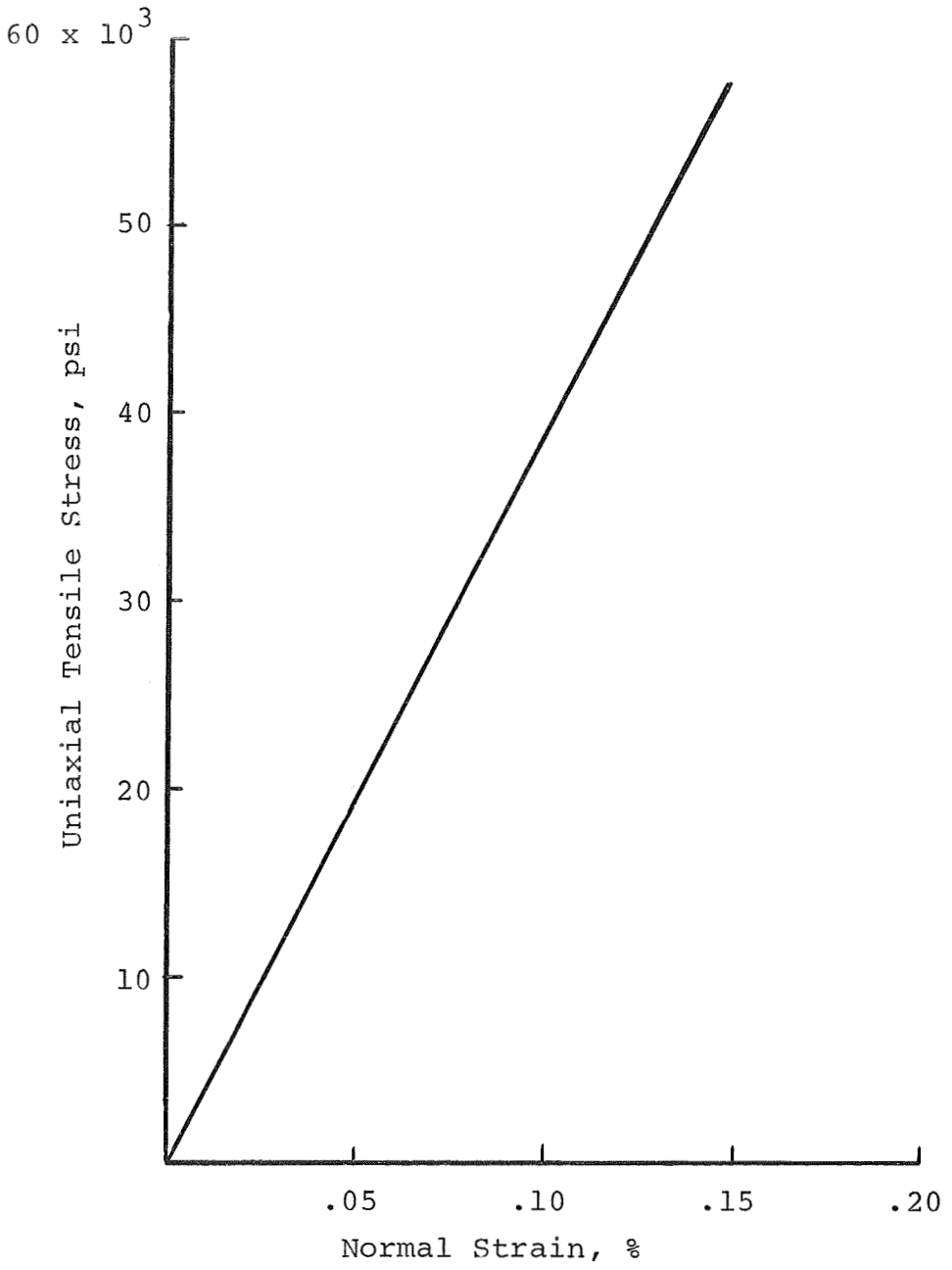


Figure 20. Stress-Strain Curve for Specimen 161-4A, Boron-Titanium.

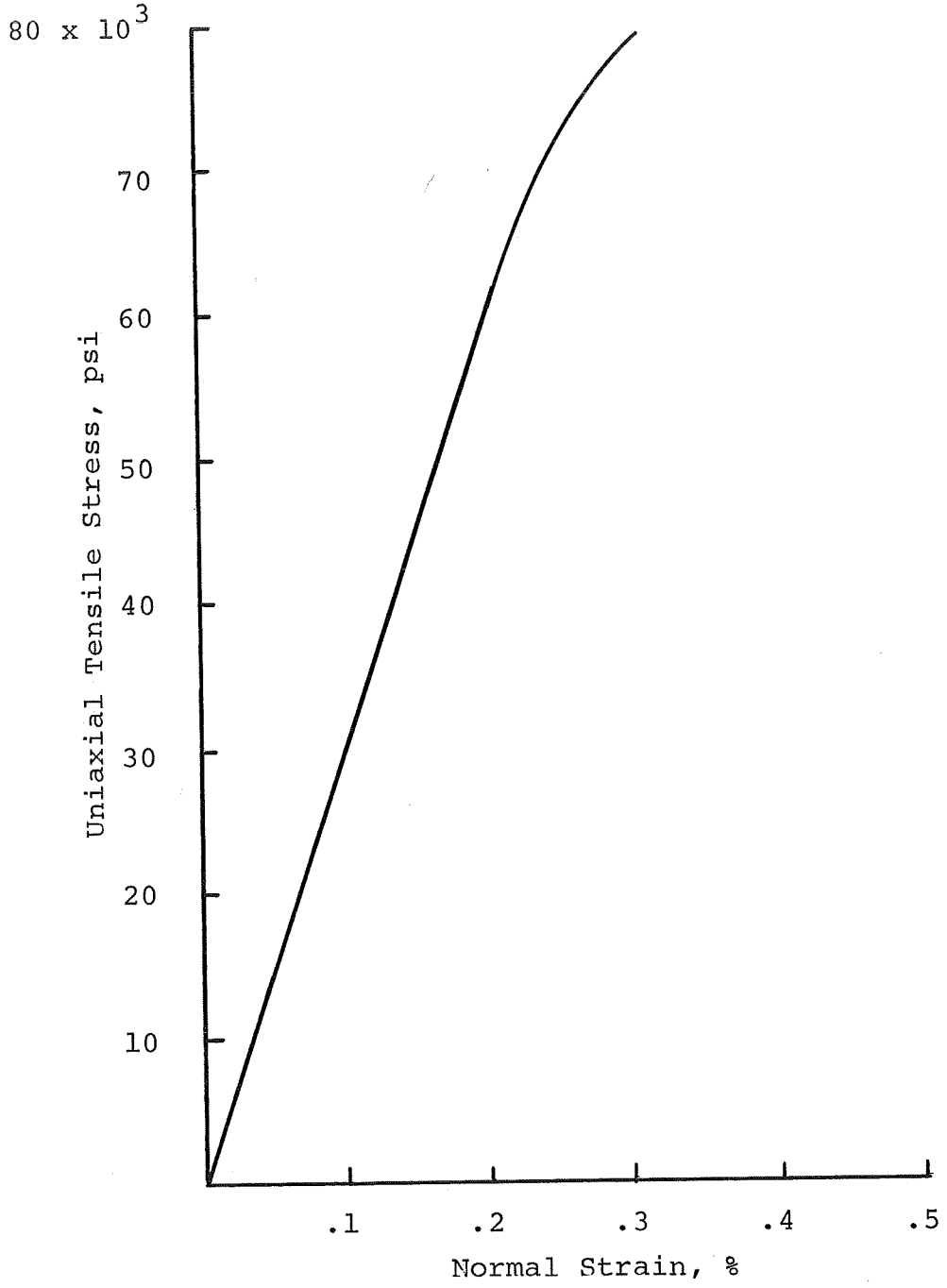


Figure 21. Stress-Strain Curve for Specimen 162-2A, Boron-Titanium.

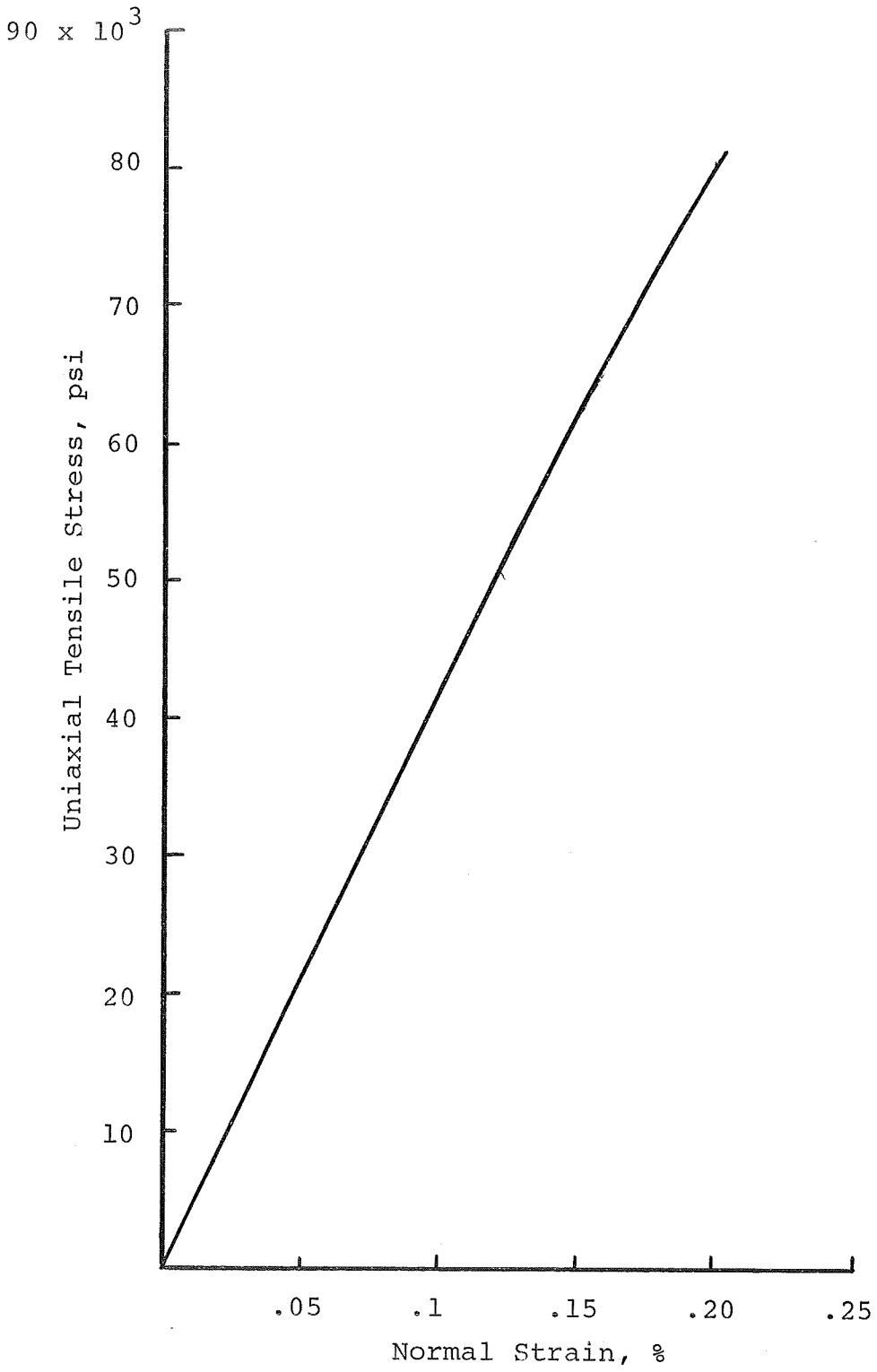


Figure 22. Stress-Strain Curve for Specimen 162-2B, Boron-Titanium.

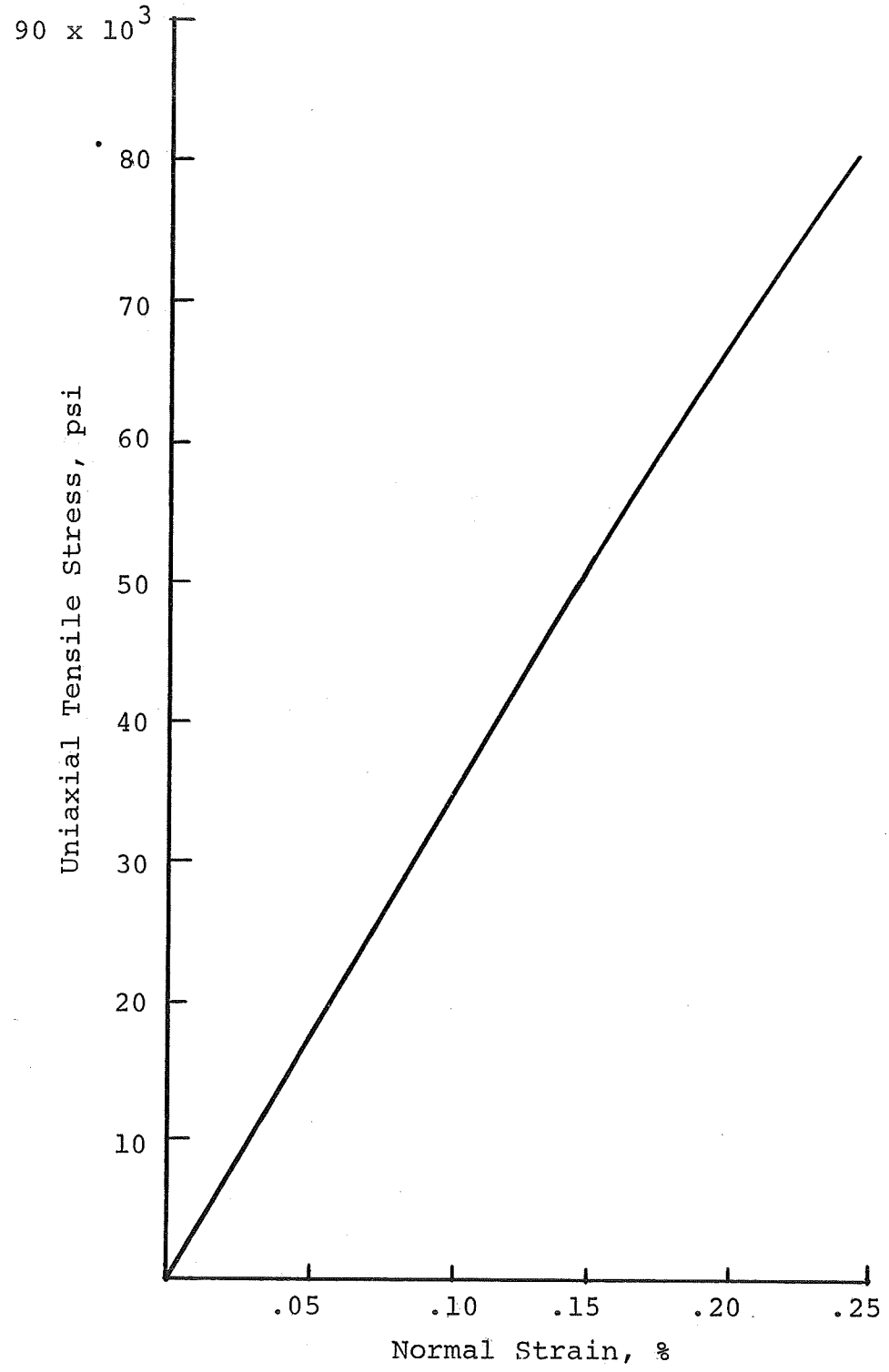


Figure 23. Stress-Strain Curve for Specimen 162-3A, Boron Titanium.

Table IX

Tensile Strength of Boron Coated Titanium Foil Coupons

Coupon No.	Width inch	Coupon Thickness mil	Boron Thickness mil	Total Sample Thickness mil	Fracture Force Pounds	Tensile Strength kpsi
161-1A	0.64	0.35	0.59	0.94	28	46.5
161-1B	0.64	0.35	0.59	0.94	30	49.9
161-2A	0.64	0.44	0.62	1.06	41	60.4
161-2B	0.63	0.44	0.62	1.06	36	53.9
161-3A	0.63	0.38	0.67	1.05	34	51.4
161-3B	0.63	0.38	0.67	1.05	43.5	65.7
161-4A	0.64	0.50	0.70	1.20	44	57.3
161-4B	0.64	0.50	0.70	1.20	32	41.7
162-2A	0.75	0.35	0.24	0.59	35	79.1
162-2B	0.75	0.35	0.24	0.59	36.5	82.5
162-3A	0.75	0.38	0.24	0.62	37.3	80.2

The work carried on in this program for each of these materials is described below.

The tensile strength of the boron coatings may be estimated in two ways. Firstly, the stress-strain curves may be used to determine the strain value at which the boron-titanium sample departed from elastic behavior (the proportional limit). If this strain is less than the elastic limit of titanium it may be assumed that the cause for non-elastic behavior of the composite was that the boron coating had failed. The boron strength could then be calculated from the product of the measured proportional limit strain and the known modulus of the boron.

A second possible way to calculate the strength is by the Rule of Mixtures. This procedure, however, is open to a number of objections -- particularly when the coatings are thin and there is little difference in the measured strengths of the coated and uncoated samples. Nevertheless, both procedures are presented in Table X.

The results presented in Table X indicate that the strength of the boron coating deposited on titanium at 550^{0}C ranged from about 60 x 10^3 psi to 110 x 10^3 psi -- based on the analysis of the stress-strain data. The thinner coatings gave the higher strengths. The Rule of mixtures gave a range of 10.1 x 10^3 psi to 77.9 x 10^3 psi. It is likely that the former analysis is the better.

While these data did not yield high boron strengths, the results were encouraging in that the procedure appeared to be feasible. It opened the possibility of measuring the coating strengths and investigating the nature of the strength controlling factors.

It appeared likely that one of the most important variables affecting the mechanical properties of the boron and boron

Table X

Calculated Strengths of Boron Deposited on Titanium at 550°C

1) From Proportional Limit Strain

Sample	Proportional Limit* Strain %	Calculated Strength 10^3 psi	Remarks
3176-161-1A	0.115	63	Failed in grip
" " 2A	0.14	77	
" " 3A	0.12	66	
" " 4A	0.16	88	
3176-162-2A	0.20	110	Failed in grip
" " 2B	0.17	93	
" " 3A	0.16	88	

*The proportional limit of the titanium substrate was measured to be 0.28 and 0.32% (two samples).

2) From Rule of Mixtures

Sample	Calculated Strength* 10^3 psi
3176-161-1A	23.2
" " 1B	28.6
" " 2A	42.4
" " 2B	31.3
" " 3A	31.9
" " 3B	54.3
" " 4A	37.0
" " 4B	10.1
3176-162-2A	69.6
" " 2B	77.9
" " 3A	71.3

*Based on the average strength of the titanium substrate of 85.7 x 10^3 psi.

carbide deposits would be the temperature of the substrate during deposition. Work on the titanium was limited to about $600^{0}C$ because at higher temperatures titanium-boron reactions become significant. For this reason the next substrates considered were tungsten and tantalum.

Work with tungsten appeared an attractive possibility because it would offer the opportunity of comparison work with the boron filament results.

However, thin tungsten foil was found to be very difficult to handle. Attempts to prepare test specimens from strips of one mil thick material were not successful. Annealing of the strip, or sometimes even cutting the strip from the supply sheet, generated a characteristic right angle crack pattern in the material. This effect is shown in Figure 24. Because of this behavior, no further work was done with tungsten. The substrate used for the higher temperature deposition coatings was tantalum as described below.

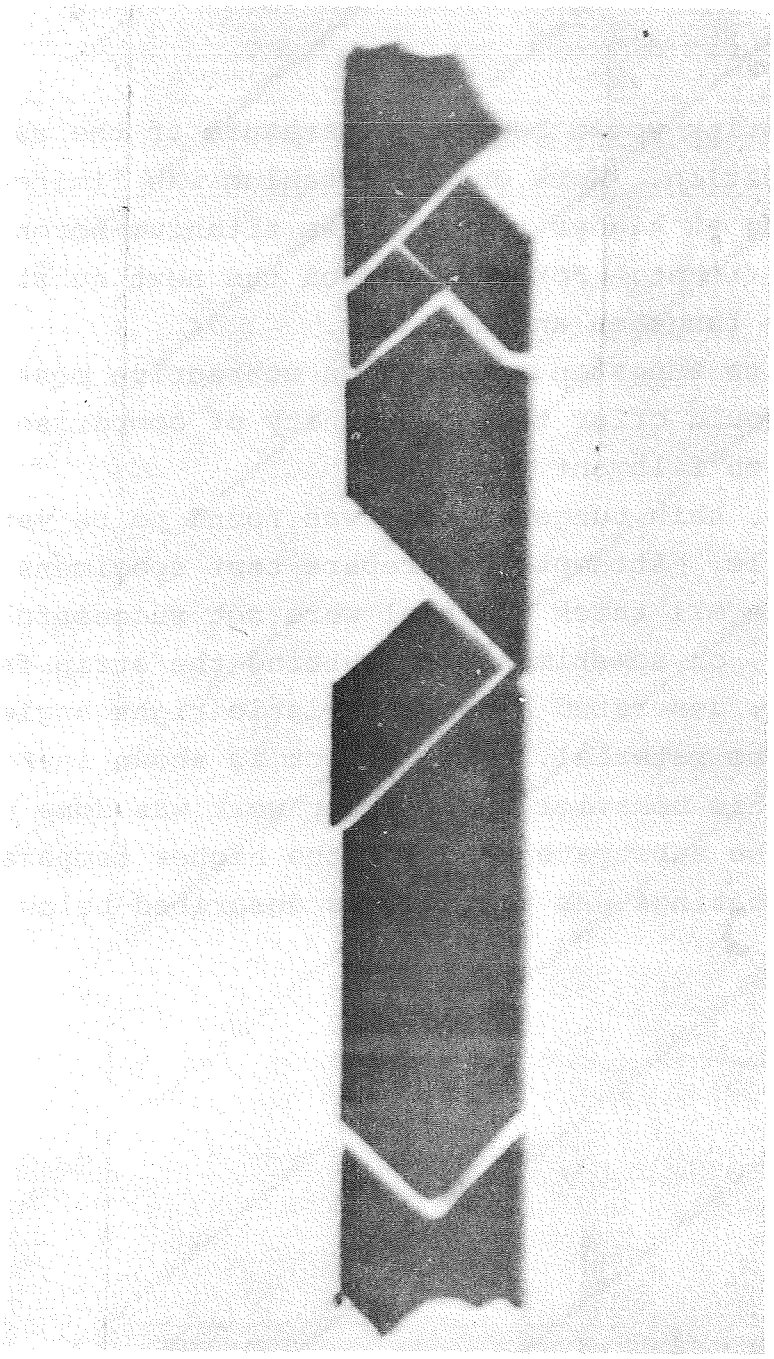


Figure 24. Crack Effect Found in Tungsten Foil. X 1.35.

Preparation and Testing of Tantalum Specimens

Boron was deposited on strips of tantalum foil in order to investigate the effect of deposition temperatures above 700°C on the strength of ceramic coatings. One of the "flip-flop" modules was modified to permit specimen strips to be resistance heated to temperatures up to 1350°C while the module was being flipped back and forth. The module is shown after modification in Figure 25.

As with the titanium, the strength of the uncoated metal was first determined. Individual test size coupons, cut from one mil tantalum foil, were mounted in the modified module and were annealed in vacuum at various temperatures for different intervals of time to determine the conditions which would yield a reproducible tensile strength in the material. The coupons were solvent cleaned and chemically polished before they were mounted in the module. After annealing, the specimens were fitted with strain gauges and were tested in tension. The annealing conditions and the test results for these uncoated specimens are shown in Table XI. The stress-strain curves are shown in Figures 26 through 30. The data indicated that a temperature of 1000°C produced no significant change in the tensile strength of the tantalum between exposures of 5 minutes and one hour. Temperatures from 1150°C to 1250°C produced a reduction in the tensile strength. There was some evidence (specimen 176) that higher temperatures (1320°C) increased the tensile strength presumably because of conversion of the tantalum into higher strength compounds (oxides, etc.) by reaction with the residual gases in the vacuum system. Two sets of conditions, however, appeared to

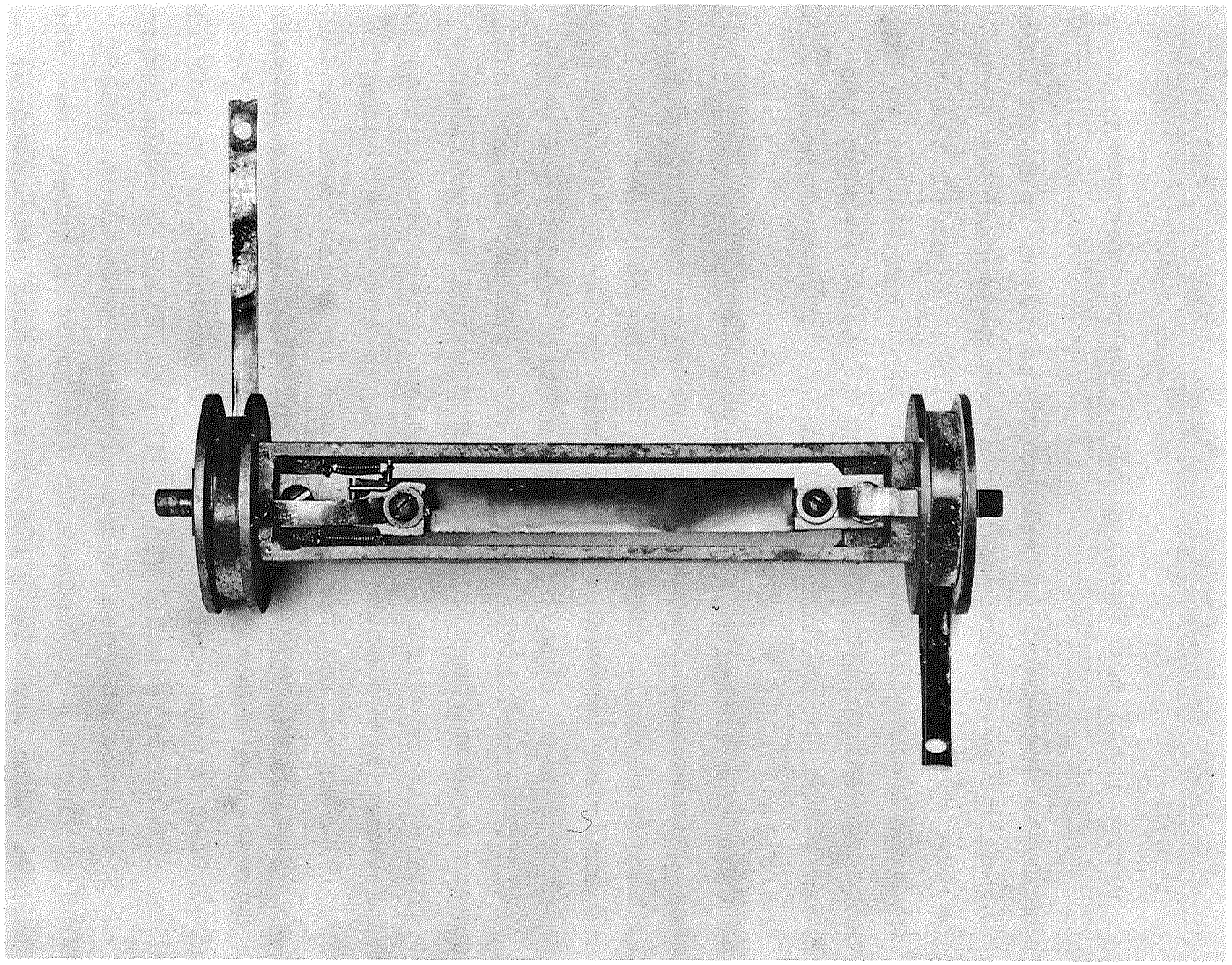


Figure 25. Modification of "Flip-Flop" Module for Resistance Heating. X 0.45.

Table XI

Tensile Strength of Annealed Uncoated Tantalum Specimens

Specimen No.	Width inch	Thick mils	Fracture Force lbs	Tensile Strength kpsi	Anneal Temp ^{0}C	Anneal Time min
150-36	0.50	1.09	55	101	None	None
173	0.50	1.09	57	105	1000	60
176	0.50	1.10	77	140	1320	5
177	0.50	1.09	53	97	1200	6
178	0.50	1.12	46	82	1150	5
179	0.50	1.13	46	81	1250	6
180	0.50	1.12	58	103	1000	5
181	0.50	1.11	44	79	1150	30

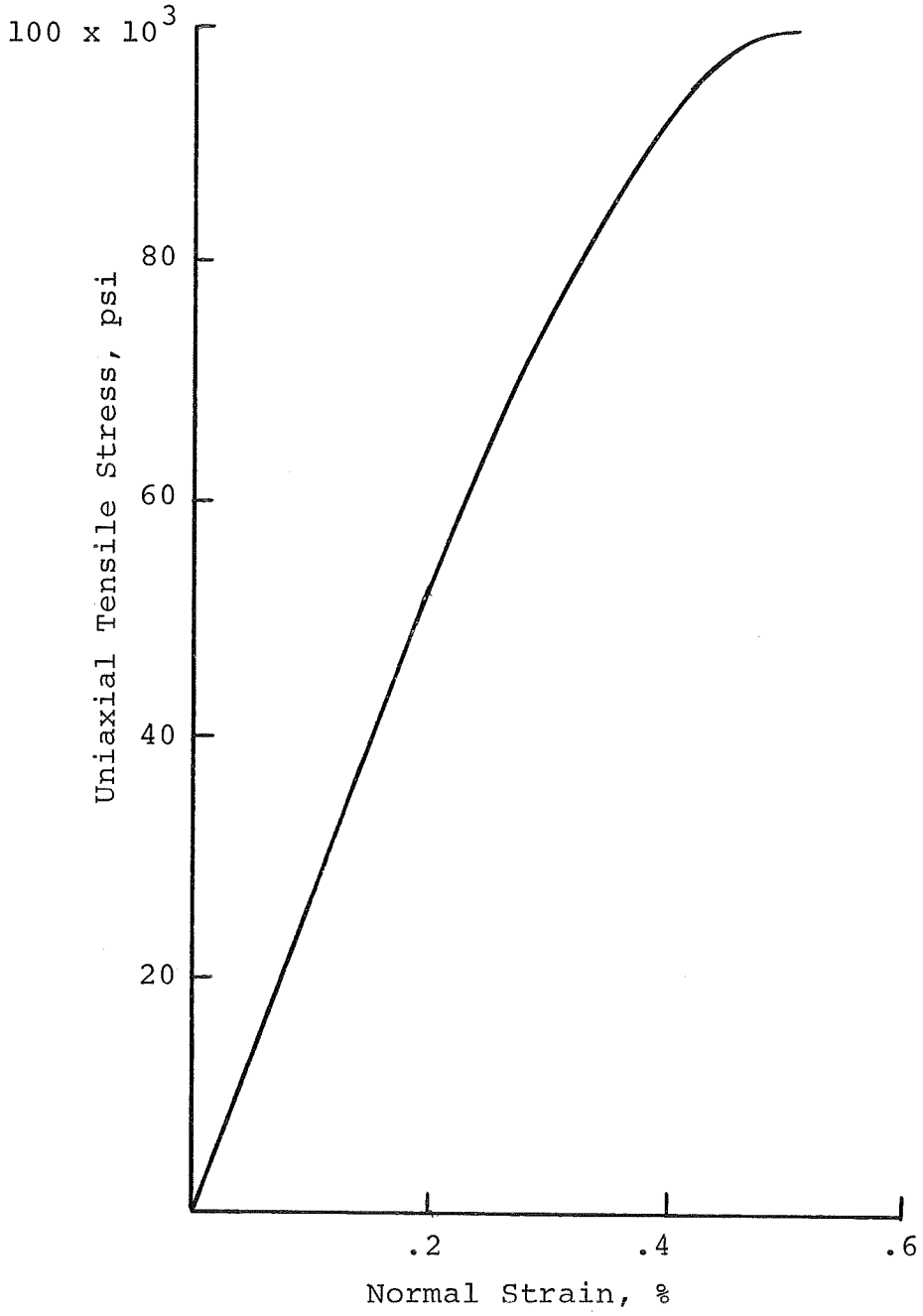


Figure 26. Stress-Strain Curve for Specimen 150-36, Annealed Tantalum.

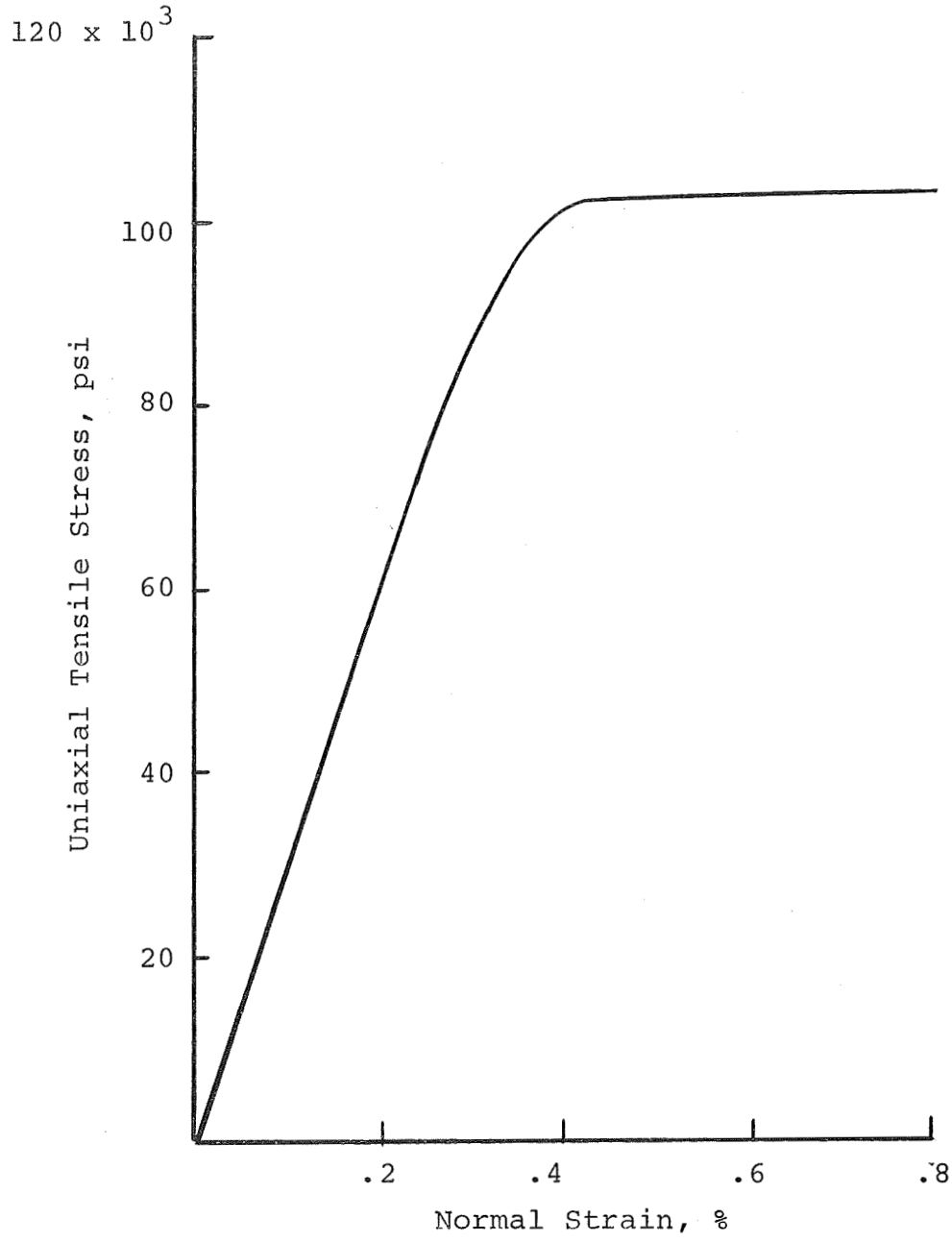


Figure 27. Stress-Strain Curve for Specimen 173, Annealed Tantalum.

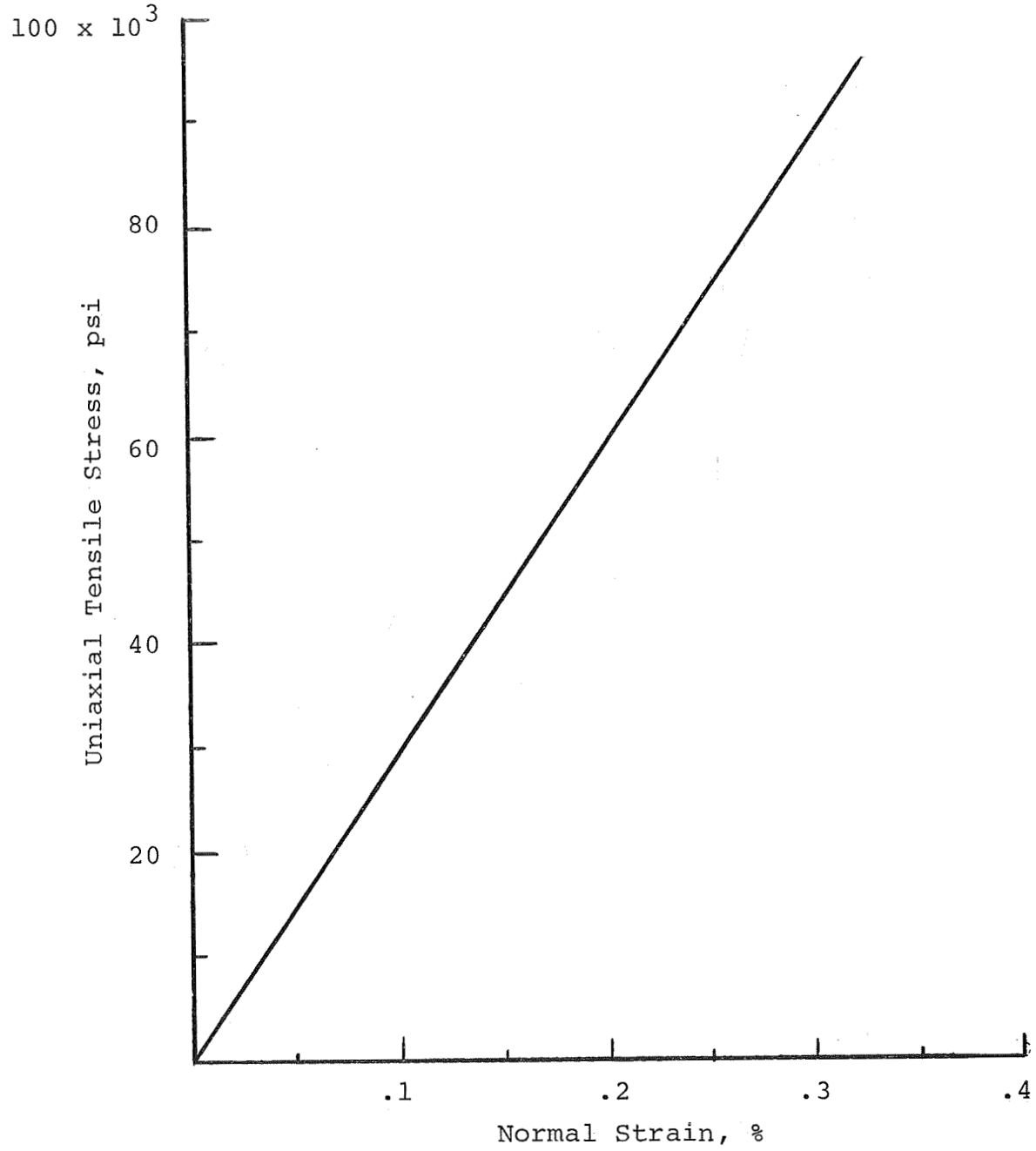


Figure 28. Stress-Strain Curve for Specimen 177, Annealed Tantalum.

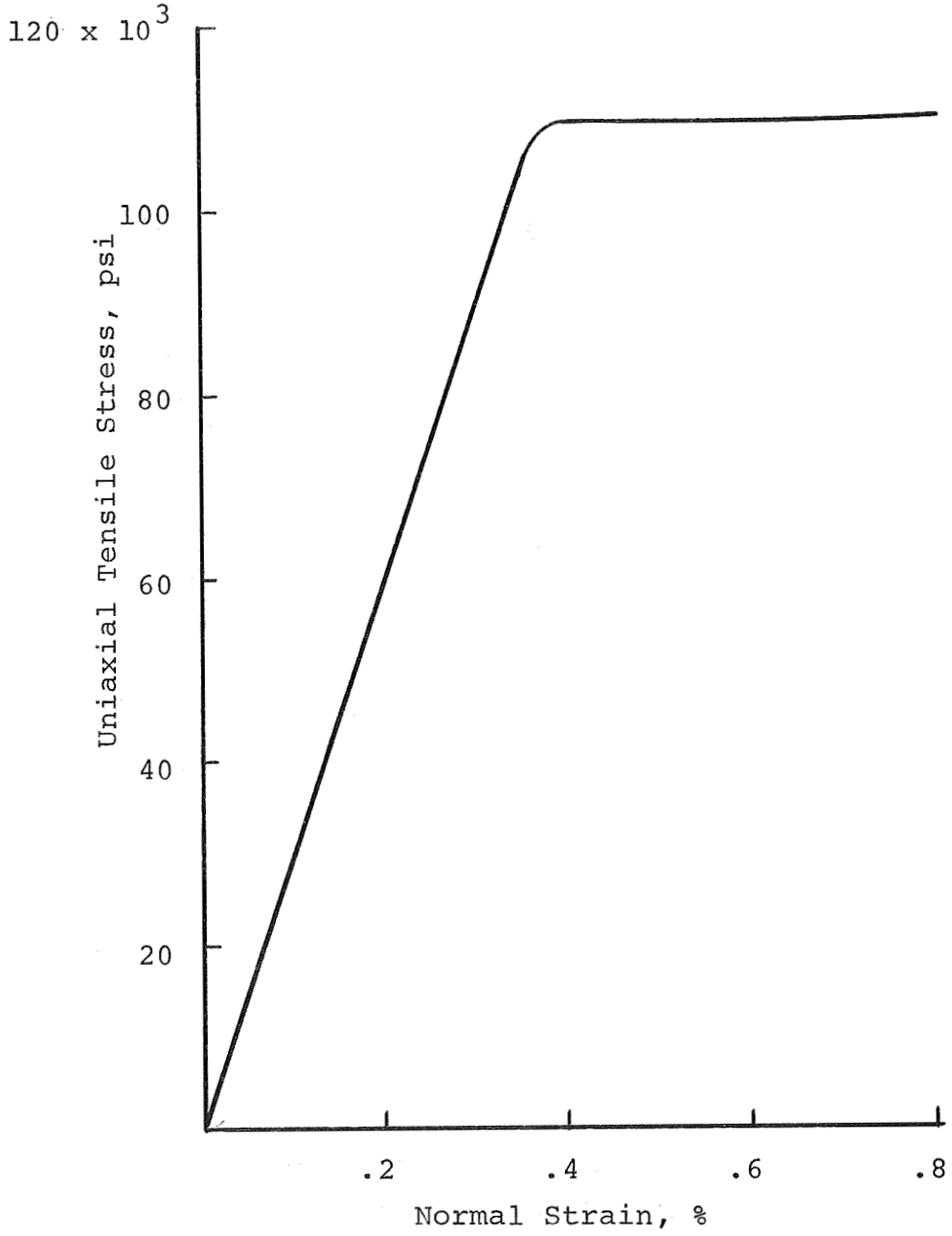


Figure 29. Stress-Strain Curve for Specimen 180, Annealed Tantalum.

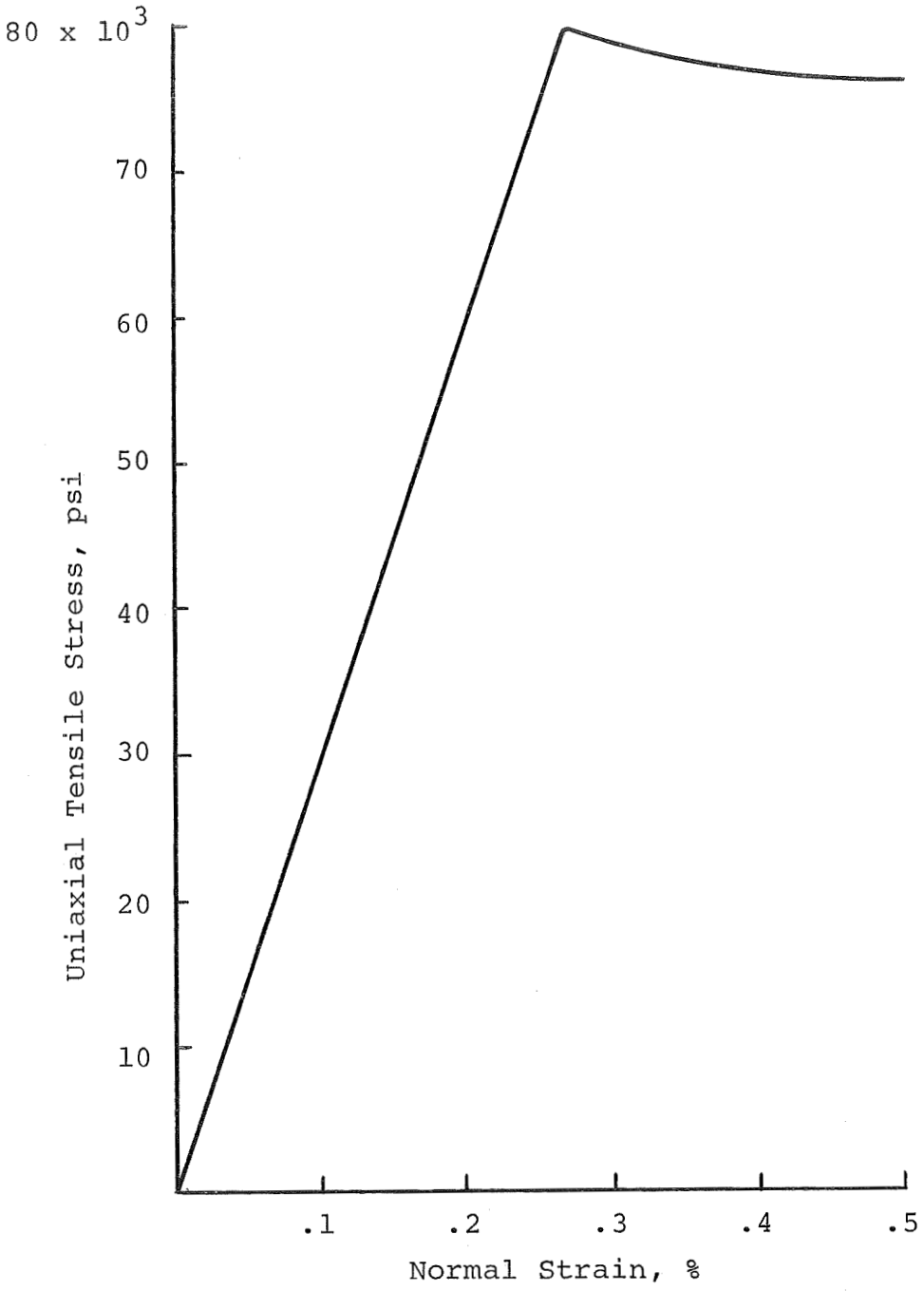


Figure 30. Stress-Strain Curve for Specimen 181, Annealed Tantalum.

give tensile strengths which were relatively reproducible: firstly, temperatures up to 1000^{0}C for one hour and secondly, a temperature of 1150^{0}C also for periods up to one hour. These two sets of annealing conditions were used in preparing coated tensile specimens.

Three coated specimens were prepared. Additional specimens were planned but not completed because of time limitations. While details of the preparation procedure used for each specimen differed, the general procedure was the same for all and is illustrated by the following description.

A strip of tantalum foil was prepared in the same manner as for the uncoated specimens and was then mounted in the "flip-flop" module. The coating chamber was evacuated to a pressure of 1×10^{-5} torr and the strip was annealed at either 1000^{0}C for 60 minutes or 1150^{0}C for 30 minutes. The strip temperature was then adjusted and module oscillation was started. With the module flipping back and forth, the shutter was opened to expose the specimen strip to the boron vapor source. During the coating period of 15 to 25 minutes each side of the specimen was exposed alternately to the boron vapor for 5 second intervals. After coating was completed, the shutter was closed and the specimen was cooled to room temperature in vacuum before removing it from the coating chamber. The specimen was sprayed at once with a very thin protective coat of clear acrylic varnish.

Strain gauges were mounted on the three specimens. The exposure conditions, the composition of the coated specimen, and the test results for the individual samples are shown in Table XII. After the tensile tests were completed, a section of each tested sample was mounted for polishing, and examination

Table XII

Tensile Strength and Composition of Annealed and Coated Tantalum Specimens

Specimen No.	Width inch	Thick inch	Anneal Temp. ^0C	Anneal Time min	Coating Time min	Ta Thick mil	Ta_xB_y Thick mil	B Thick mil	Total Thick mil	Fracture Force lbs	Tensile Strength kpsi
174	0.51	1.08	1000	60	15	0.84	0.24	-	1.08	60	109
183	0.50	1.11	1150	30	25	0.86	0.24	0.60	1.70	54	64
186	0.50	1.11	1150	30	25	1.07	0.04	-	1.11	56	101

by optical microscopy. The section views are shown in Figures 31 through 33. The layers which made up the specimens were clearly evident. The thickness of each layer could be estimated by scaled measurement from the photomicrographs. The thickness data are included in Table XII.

The core and main portion of each of the specimens was tantalum metal. In all three samples this core was covered on both sides with a layer of material which appeared to be the product of a reaction between the boron vapor and the outside of the tantalum metal specimen. Specimen 174, for instance, was not coated with the usual shiny black deposit normally associated with boron. The coating instead had a bronze metallic lustre. In Table XII these layers have been designated as Ta_xB_y. In specimen 183 there was an additional layer on each side. This layer appeared to be unreacted boron and has been so designated in the table.

In the course of this work, considerable difficulty was experienced in measuring and controlling the temperature of the substrate during the coating operation. Measurements of the temperature of the substrate during the annealing step were carried out after calibrating an optical pyrometer for the annealing conditions. On the other hand during evaporation, energy reflected from the source and variations in the reflectivity of the sample being coated made optical pyrometer measurements highly ambiguous. In the later experiments (183 and 186) attempts were made to hold the temperature constant by maintaining a constant resistance in the foil being coated (the resistance of pure boron was expected to be considerably higher than the tantalum substrate for the coating thicknesses planned). While apparently feasible, this technique was not refined to a degree where reliable

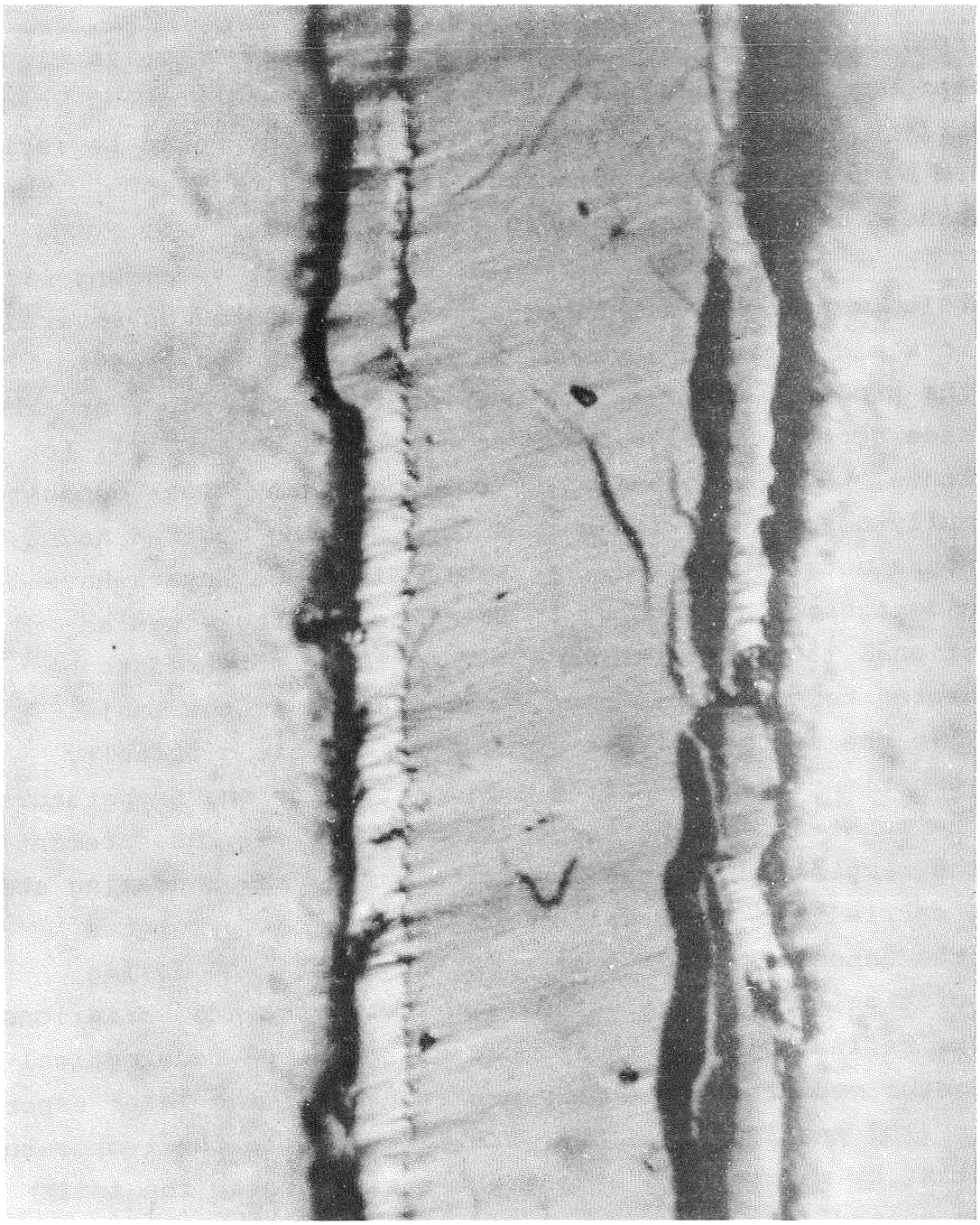
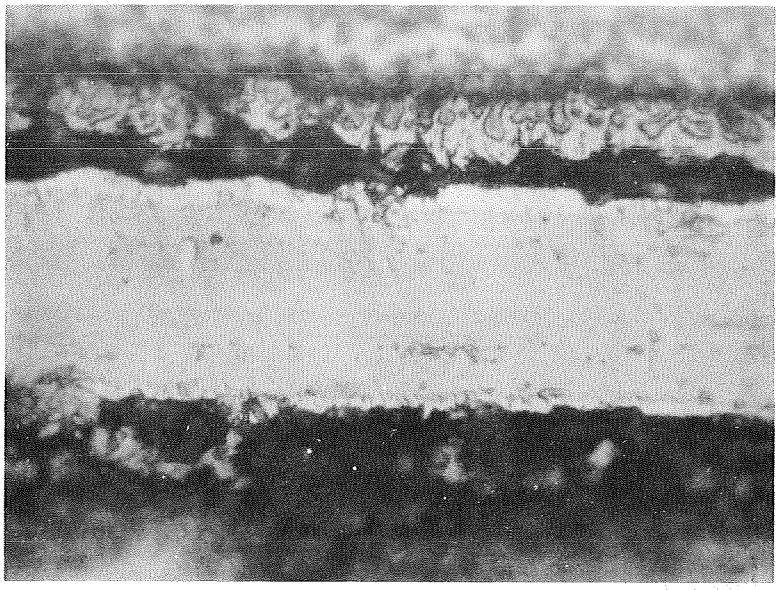
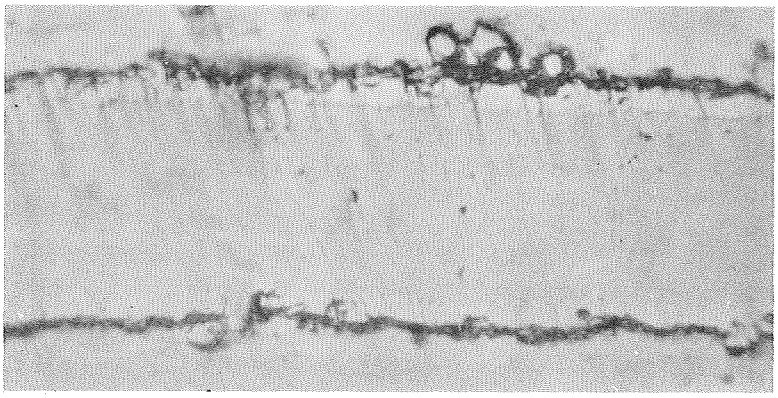


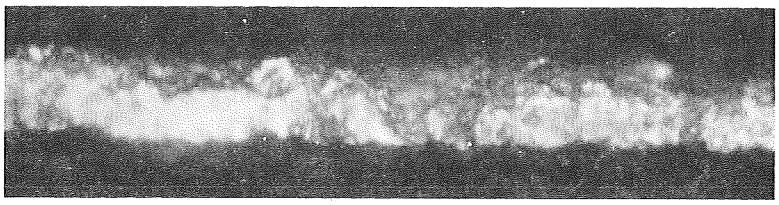
Figure 31. Sectional View of Specimen 174, X 1400, Boron-Tantalum.



a. Entire Thickness of Specimen. X 800.



b. Specimen with Outer Coating Removed. X 775.



c. Outer Coating Only. X 800.

Figure 32. Sectional View of Specimen 183, Boron-Tantalum.

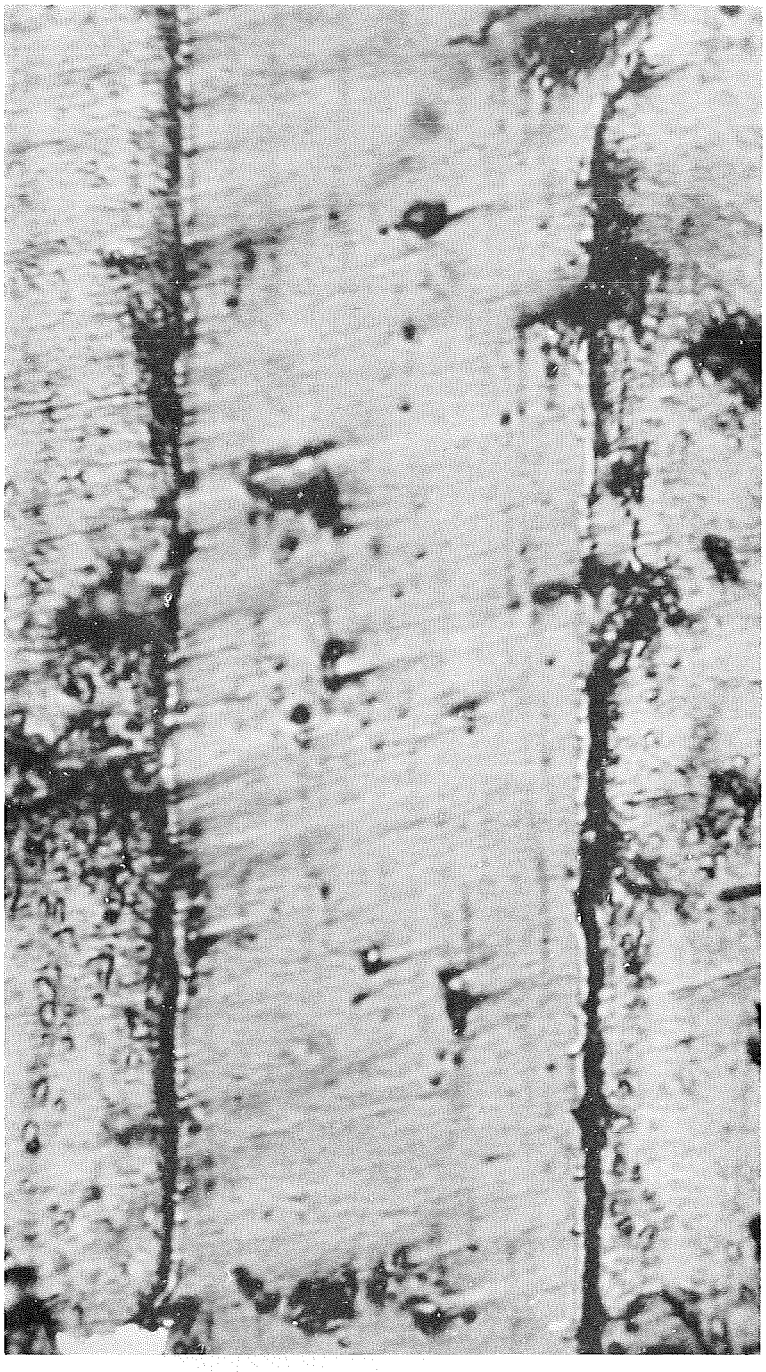


Figure 33. Sectional View of Specimen 186, X 1400, Boron-Tantalum.

substrate temperature control was maintained. The results obtained were therefore questionable. Nevertheless, temperatures were apparently in excess of that required to hold the interaction of the boron and tantalum to low values.

Examination of the stress-strain curves for the coated samples indicated departures from elastic behavior for all three samples at about 0.17% strain. Assuming the modulus of the coating to be 55×10^6 psi, the coating strength would then be estimated at about 90×10^3 psi. The general evidence suggested, however, that this was associated with the failure of the interaction product and not with the boron.

Although the work described above indicated that boron could be vacuum evaporated onto metallic foils at elevated temperatures the techniques were not refined to the degree to obtain satisfactory strength measurements. The so called "flip-flop" procedure, however, does appear to be a feasible method of producing coated foils to which strain gauges may be attached for detailed analysis of the mechanical properties of the deposit-substrate combination. Further work is required to:

1) Refine the procedure for reliable temperature measurement and control.
2) Coat a number of substrates with boron over a wide temperature range.
3) Measure the strength of the deposit and ascertain the strength controlling factors.

It is hoped that this course will permit an evaluation of the relative importance of the many variables which may affect the tensile properties of the vacuum evaporated coatings and lead to significant increases in the strength.

CONCLUSIONS

The main conclusions reached during this investigation may be summarized as follows:

1) The polyimide film (¼ mil) used as a substrate for the vacuum deposition of boron and boron carbide showed some asymmetry when heated. It shrank about 2.6% across the width of the film after heating to 350^{0}C for 20 minutes. There was no dimensional change in the direction of the main length of the film.

2) The polyimide film had a number of surface defects and regions of stress. Defects such as holes in the film or lumps on the surface of the film were replicated by the vacuum deposits. These defects initiated cracks in the coating but were not the main source of crack nucleation.

3) The most important crack nucleating defects observed were those associated with spit marks and small droplets of boron and boron carbide embedded into the vacuum deposit.

4) Extended vacuum degassing of the polyimide substrate before coating did not significantly increase the adherence of the vacuum deposits. The degassing treatments used, however, significantly reduced the tensile strength of the polyimide film, decreased its tear resistance and reduced the elongation limit.

5) There were some indications that increasing the substrate temperature during deposition resulted in materials which gave higher composite strengths.

6) Techniques which were developed for vacuum coating both sides of single strips of thin substrate materials permitted specimens to be prepared which were flat, uncracked

and sufficiently strong to permit handling, application of strain gauges and direct tensile testing.

7) Direct tensile tests of small flakes of boron carbide obtained by removing the substrate materials gave strength values of in the range 40,000 - 131,000 psi. Thinner flakes were stronger than the thicker flakes.

8) Preliminary work was completed for the deposition of boron on titanium and tantalum foil substrates at elevated temperatures -- up to 1100^{0}C. Stress-strain behavior of specimens resulting from the initial tests indicated that the boron films evaporated onto titanium substrates at about 600^{0}C had strengths in the range 63,000 - 110,000 psi. The results obtained on the evaporation of boron onto tantalum at 1000^{0}C were complicated by chemical interaction between the tantalum and boron.

The main result of the overall program was to develop practical methods for the direct measurement of the strength of thin vacuum-deposited films of boron and boron carbide and to identify some of the defects which affect the strength of these films. Further work is required to control the process variables so as to reduce the defect density and increase the strength of the deposits. Moderate increases in tensile strength combined with the presently obtainable values for elastic modulus, interlaminar shear strength, torsional modulus, and compressive strength would yield a unique composite material with a number of potential areas of application in space structures.

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